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Technical Report No. VIII

Research performed in the period Oct., 1953–Oct., 1954

RADIOFREQUENCY SPECTROSCOPY

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Department of Chemistry and Chemical Engineering,

University of Illinois, Urbana, Illinois

Distributed April, 1955

CONTENTS

Electron Distribution in Molecules. IV. Phosphorus Magnetic Resonance Shifts*

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(Received August 28, 1953)

Chemical shifts in the phosphorus nuclear magnetic resonance absorption have been measured in twenty compounds. The shifts arise from differences in the magnetic shielding of the phosphorus nuclei by electrons, and the values observed are interpreted qualitatively in terms of the molecular electronic structures. The range in shifts is 7×10^{-4} which is somewhat larger than observed for fluorine on which more extensive data are available. The phosphorus resonance shifts fall into two distinct groups one of which contains compounds with trivalent phosphorus and the other, pentavalent. The shifts in pentavalent compounds fall in a relatively narrow range, generally with greater nuclear magnetic shielding than in the trivalent. The resonance shifts between similar or homologous compounds can be accounted for by considering changes in the importance of ionic and double-bonded electronic structures.

INTRODUCTION

VARIATIONS in the location of a nuclear magnetic resonance with chemical constitution were first reported by Knight[1] for P^{31}. Although no details were given, his estimated magnitude of 0.01 percent for the effects is consistent with the measurements reported herein. Ramsey's[2] theoretical analysis ascribes the variations to magnetic shielding of nuclei by the molecular electrons, whose motions interact with the applied magnetic field. A change in electron distribution with chemical constitution changes the magnetic shielding of a nucleus and chemically shifts its resonance position. Thus, in principle, information about the electronic structures of molecules can be obtained from chemical shift data. Although detailed calculations have been made[2] only for H_2, data and semi-empirical analyses have been given for a large number of proton and fluorine chemical shifts in various types of compounds.[3-6]

If the chemical shifts are to be measured accurately, the resonance lines should be narrower than the shifts, and this usually requires that the sample be liquid to minimize internuclear magnetic dipole broadening. Also, as the resonances can be broadened by electric quadrupole interactions, the best nuclei for this type of experiment are those with spins of $\frac{1}{2}$, in which case the electric quadrupole moment is zero. Furthermore, the nuclei must exist in sufficient isotopic abundance and with a large enough magnetic moment to give measurable absorption. Fluorine and hydrogen nuclei are well suited for this type of experiment as evidenced by the results already obtained. Phosphorus has one stable isotope P^{31}, and it meets the requirements for

shift measurements rather well as it has a spin of $\frac{1}{2}$ and a sizeable magnetic moment.

The main objective of this note is to summarize the phosphorus resonance shifts observed thus far and to discuss their utility in determining molecular differences in bond type. Some of the phosphorus resonance shifts we have observed were given in connection with the multiplet resonance lines arising from the electron coupling of nuclear spins.[7] Also, Dickinson[8] reported earlier the resonance shifts in PCl_3, PBr_3, and $POCl_3$ with respect to H_3PO_4 (aq.); our results agree with his within experimental error. In considering the phosphorus resonance shifts we encounter two factors not present in case of fluorine and hydrogen. First, phosphorus is multivalent and second, it has two stable valence states. Although these factors complicate any interpretation, one may be led to a better understanding of multivalent bond structures in the attempt.

EXPERIMENTAL METHOD

The experimental details were similar to these described earlier.[3,7] The resonances were observed at about 6365 gauss, using an rf bridge, 30 cps modulation, and oscilloscope display. The resonance shifts were measured at a fixed radio-frequency as the difference in applied field to center the resonance lines of the compound and the reference on the oscilloscope. The multiplet structures observed in many of the resonances were symmetrical and the center was used in determining the resonance shift, as is justified theoretically.[7] Usually a set of ten measurements was made by placing successively the sample and reference compound in the same coil. The order was reversed for half the measurements so any constant drift in frequency or field would cancel out. Statistical errors were the order of ±0.006 gauss, and systematic errors up to one percent may be present in addition.[3]

Compounds do not need to be extremely pure for chemical shift measurements, and commercial

[1] W. D. Knight, Phys. Rev. 76, 1259 (1949).
[2] N. F. Ramsey, Phys. Rev. 78, 699 (1950); 86, 243 (1952).
[3] H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. 19, 1259 (1951).
[4] Gutowsky, McCall, McGarvey, and Meyer, J. Am. Chem. Soc. 74, 4809 (1952), I.
[5] L. H. Meyer and H. S. Gutowsky, J. Phys. Chem. 57, 481 (1953), II.
[6] Meyer, Saika, and Gutowsky, J. Am. Chem. Soc. 75, 4567 (1953), III.

[7] Gutowsky, McCall, and Slichter, J. Chem. Phys. 21, 279 (1953).
[8] W. C. Dickinson, Phys. Rev. 81, 717 (1951).

samples were used without further purification. The $Cl(CH_2)_3PCl_2$ and $C_2H_5OPOCl_2$ were kindly provided by Dr. D. R. Martin; the sources of the other samples have been given.[7] The shifts in PH_3 and PF_3 were measured in the liquids at about $-90°C$. Yellow phosphorus (P_4) and P_4S_3 were measured at room temperature in the solid state, the latter with a narrow band amplifier. The other compounds were liquid at room temperature and were measured as such.

In this paper we define the chemical shifts of P^{31} as $10^5 \times (H_c - H_r)/H_r$ where H_c and H_r are the magnetic fields required for resonance in the sample and in a reference, respectively, at a fixed radio-frequency. Aqueous H_3PO_4 was chosen as an arbitrary reference, as it gives a strong, narrow resonance and is readily available. With this definition, more positive shifts correspond to greater magnetic shielding of the nucleus. The δ values used in discussions of fluorine[4,5] and proton[5,6] shifts are defined similarly, but the sign is reversed so that changes in δ correspond to changes in the charge on the atom.

RESULTS AND DISCUSSION

The phosphorus resonance shifts observed are given in Table I, with trivalent and pentavalent compounds listed separately. Before discussing individually several of the various types of compounds, some general observations will be given.

The pentavalent compounds, excluding HPF_6, have phosphorus shifts clustered in the narrow range from 2 to -3. In HPF_6, which has a higher shielding of 11.8, the structure is octahedral, sp^3d^2, while the other pentavalent compounds use sp^3d orbitals. In Ramsey's theory[2] the shielding increases with the electrostatic potential at the nucleus and is reduced by a second-order paramagnetism which arises in part from the lack of spherical symmetry introduced by the bonding electrons. The higher symmetry of the PF_6^- compared to the other compounds, as well as the contribution of the additional two electrons may account for the greater shielding of the phosphorus. Also, as we shall consider below, replacement of other atoms with fluorine increases the phosphorus shielding, and PF_6^- is unusual in the number of fluorines.

With the exception of P_4, PH_3, and P_4S_3, the trivalent phosphorus compounds have shielding values ranging from -9.7 to -22.2, considerably below the -3 lower limit of the pentavalent compounds. The bonding in the trivalent compounds is a combination of p^3 and sp^2, and the lower shielding most likely arises because there are fewer valence electrons and a less symmetrical electronic distribution than in the pentavalent compounds. In this connection it is of interest to note that the chlorine nuclear quadrupole coupling constants[9,10]

[9] R. Livingston, J. Phys. Chem. 57, 496 (1953).
[10] D. W. McCall and H. S. Gutowsky, J. Chem. Phys. 21, 1300 (1953).

TABLE I. Chemical shifts[a] in the P^{31} magnetic resonance.

Trivalent compounds			Pentavalent compounds		
Formula	Chemical shift	Probable error	Formula	Chemical shift	Probable error
P_4 (in CS_2)	48.8	0.02	HPF_6	11.8[b, c]	
P_4	45.0	0.03	$F_2PO(OH)$	2.01[b]	0.01
PH_3	24.1[b]	0.03	$POClF_2$	1.48[b]	0.02
P_4S_3	11.4[c]		$POCl_2F$	0.00[b]	0.02
PF_3	-9.7[b]	0.05	H_3PO_4	0.00	reference
CH_3OPF_2	-11.1[b]	0.02	$HPO(OH)_2$	-0.45[b]	0.04
P_2I_4(in CS_2)	-17.0[c]		$POCl_3$	-0.54	0.04
PI_3	-17.8	0.04	$C_2H_5OPOCl_2$	-0.64	0.06
$Cl(CH_2)_3PCl_2$	-18.2	0.07	$H_2PO(OH)$	-1.38[b]	0.06
PCl_3	-21.5	0.09	$PSCl_3$	-3.08	0.05
PBr_3	-22.2	0.11			

[a] Referred to aqueous H_3PO_4; defined as $10^5 \times (H_c - H_r)/H_r$ where H_c and H_r are the resonance magnetic fields for the sample compound and reference, respectively.
[b] The resonance exhibited multiplet structure; see reference 7 for details.
[c] The resonance was weak and the shift value is good only to ± 1.0.

demonstrate that the P—Cl bonds are considerably more covalent in PCl_5 than in PCl_3.

(a) PF_3, PCl_3, PBr_3, PI_3: In this homologous series the phosphorus shielding decreases in the order PF_3, PI_3, PCl_3, and PBr_3, with the iodide out of sequence and the fluoride shielded considerably more than the other halides. Similar trends have been noted in the proton shifts[5] in the methylene halides (CH_2X_2) and haloforms (CHX_3), and in the substituent effects[4] in benzene. The observed order reflects the presence of two opposing effects, ionic and double bond character. The P—X electronegativity difference increases on passing from PI_3 to PF_3, and the ionic bond character should increase accordingly. Also, fluorine and to a lesser extent chlorine and the larger halogens can form double bonds. So the observed shifts are compatible with the phosphorus shielding increasing as the double bond character is increased and decreasing as the ionic bond character is increased. Thus, for ionic character effects alone, the phosphorus shielding would decrease in the sequence I, Br, Cl, and F; the opposing double bond effect is greatest for F and the next for Cl, giving the observed sequence F, I, Cl, and Br. Moreover, the double bond character effect in PF_3 is very pronounced compared with the other halogens; this is consistent with the well-known chemical concept that first row atoms double bond most effectively.[11]

(b) $POCl_3$, $POCl_2F$, $POClF_2$, POF_3: In these compounds both the phosphorus and the fluorine[7] shielding increase with fluorine substitution. Pauling has proposed[12] structures for the phosphorus oxyhalides such as
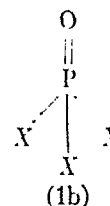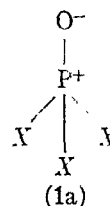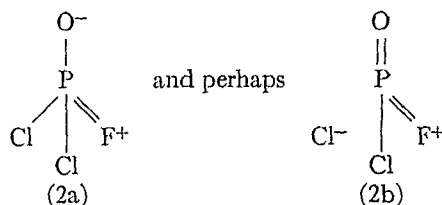

(1a)   (1b)

[11] K. S. Pitzer, J. Am. Chem. Soc. 70, 2140 (1948).
[12] L. Pauling, The Nature of the Chemical Bond, (Cornell University Press, Ithaca, New York, 1948), second edition, p. 83.

However, in order to give the observed trend in the phosphorus shifts, there must be double bond structures of the type

The increase in phosphorus shielding with fluorine substitution again reflects the greater ease with which fluorine forms double bonds, compared to chlorine. The increase in the fluorine shielding upon continued substitution is analogous to that observed in the chlorofluoromethanes;[5] competition among the fluorines makes each P—F bond less double, *increasing* the fluorine shielding; but in the polyfluoro compound the P—F bonds still have more double bond character than P—Cl bonds. Although the effects of fluorine substitution are qualitatively the same in the tri- and pentavalent compounds, the magnitudes are considerably less in the latter.

(c) $POCl_3$, $PSCl_3$: The phosphorus shielding is higher in $POCl_3$ than in $PSCl_3$. If we consider the analysis above as valid, this provides a direct verification that oxygen forms double bonds more readily than does sulfur and that P=O structures are important in the oxyhalides, as expected.[11] By analogy with the trihalides, if the ionic forms (1a) were the most important in both $POCl_3$ and $PSCl_3$, the greater electronegativity difference in P—O would reduce the phosphorus shielding below that in the sulfide. The double bond structure (1b) must be the main structure in $POCl_3$ to account for the greater shielding observed in it.

(d) $H_2PO(OH)$, $HPO(OH)_2$, $PO(OH)_3$: The phosphorus shielding increases as hydrogens on the phosphorus are replaced by OH groups. This suggests the importance of structures like P—O—H and P⁻=OH⁺. Confirmation is provided by the shielding of the protons attached to the phosphorus,[7] which is greater in $HPO(OH)_2$ than in $H_2PO(OH)$. On the basis of the structures postulated, there should be a greater negative charge on the phosphorus in $HPO(OH)_2$ than in $H_2PO(OH)$, reducing the ionic character of the P—H bonds and increasing the proton shielding (i.e. decreasing the proton δ values[6]), as observed.

(e) F_3PO, $F_2PO(OH)$, $FPO(OH)_2$, $PO(OH)_3$: This set of compounds is similar to the hydrogen-hydroxyl series in (d) above and also the phosphorus oxyfluorochlorides in (b). The phosphorus resonance could be found only in $F_2PO(OH)$ and $PO(OH)_3$, with the phosphorus shielding greater in the fluorine derivative. Furthermore, the fluorine shielding increases with fluorine substitution. These trends are analogous to those in (b) and (d) and are explainable in the same manner, assuming P⁻=F⁺ electron distributions are relatively more important than P⁻=OH⁺.

(f) P_4; P_4S_3; PH_3: As remarked in the initial discussion, the phosphorus shifts are very large in these compounds, particularly in P_4. P_4 and P_4S_3 have abnormally small bond angles; the associated strain no doubt affects the bond hybridization and could be responsible for the observed effects. The high value in PH_3 could result from ionic forms P⁻H⁺, which increase the charge on the phosphorus and should increase its shielding. A sizeable chemical shift exists between $P_4(s)$ and P_4 (in CS_2) indicating there are significant intermolecular effects in the solid, as was evidenced earlier by relaxation of the infrared selection rules in the solid.[13]

In conclusion it is instructive to make an intercomparison of the influence of bond type upon the magnetic shielding of phosphorus, fluorine, and hydrogen nuclei. In the case of phosphorus we have seen that an increase in double bond character increases the nuclear shielding, while for fluorine the shielding is decreased.[5] In a double bond the charge distribution is P⁻=F⁺; the changes in net formal charge are opposite for the two nuclei, as are the associated chemical shifts. On the other hand an increase in ionic character decreases the phosphorus shielding while increasing that of fluorine; but again this is consistent with the opposite charges that ionic character places upon the two nuclei, P⁺F⁻. Hydrogen does not form double bonds, and its shielding decreases with an increase in ionic bond character, R⁻H⁺; however, there are appreciable bond hybridization effects as well.[5,6] The chemical shifts in the magnetic shielding of all three nuclei appear therefore to correspond qualitatively to what we might call differences in "electron density" about the nuclei.

ACKNOWLEDGMENT

[13] H. S. Gutowsky and C. J. Hoffman, J. Am. Chem. Soc. 72, 5751 (1950).

The Nuclear Spin of Si²⁹†

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(Received January 15, 1954)

SEVERAL attempts have been made to determine the spin of Si²⁹ with either inconclusive,[1] conflicting,[2] or rather indirect[3] results. The consensus favors the value 1/2. Nuclear shell theory gives 1/2, 3/2, and 5/2 as the only possibilities.[1] We have eliminated values greater than 1, thereby establishing the spin of Si²⁹ as 1/2. This was accomplished by resolving the multiplet structure produced in the fluorine nuclear magnetic resonance by the electron coupled interaction[4] of the Si²⁹ spin with the F¹⁹ spins, using isotopically enriched Si²⁹F₄.

In pure liquid or gaseous Si²⁹F₄, the fluorine resonance should be a multiplet, with $2I(\text{Si}^{29})+1$ equally spaced components of the same intensity.[4] The SiF₄ actually used was prepared[5] from a sample of SiO₂ whose composition was given as 30, 69, and 1 percent, respectively, of Si²⁸, Si²⁹, and Si³⁰. The enriched sample of SiO₂ was supplied by the Oak Ridge National Laboratory. The spins of Si²⁸ and Si³⁰ are presumably zero so the Si²⁸F₄ and Si³⁰F₄ should give a single fluorine resonance with 31 percent of the total absorption, located at the center of the Si²⁹F₄ multiplet. The high-resolution spectrometer and experimental procedures used have been described elsewhere.[6] A typical oscilloscope photograph of the fluorine resonance observed in the liquefied sample of SiF₄ is reproduced in Fig. 1.

Figure 1 shows a symmetrical multiple resonance of three components with approximate *peak* intensities of 1:2:1. The separation of the two outer components is 46 milligauss. The number of lines observed is compatible with a spin of either 1/2
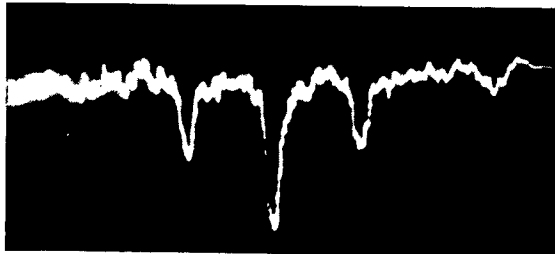
or 1. For a spin of 1/2 the predicted *integrated* absorption of the components should be 34.5:31:34.5, and for a spin of 1, 23:54:23; in the latter case the Si²⁸F₄ and Si³⁰F₄ lines overlap the center component of the Si²⁹F₄ triplet. The observed *peak* intensities correspond more closely to the spin 1 case than to the spin 1/2. However, a spin of 1 is eliminated by the shell theory; moreover, there is a convenient mechanism to explain the intensities observed.

In aqueous, concentrated H₂Si²⁹F₆ the fluorine resonance was not split by the Si²⁹ spin but was broadened to about 4 milligauss compared to 2 milligauss in H₂Si²⁸F₆. This effect[4] is produced most likely by fast chemical exchange[7] involving the fluorines. In the case of SiF₄, hydrolysis would result from a trace of water, giving HF which would catalyze exchange of the fluorines. Depending upon the exchange rate, there can be a significant reduction in the peak intensities and some broadening of the component lines. In Fig. 1 noise obscures any broadening of the outer components, but this explanation is supported by the observation that the ratio of the intensity of the outer components to that of the center line decreased at higher temperatures, for which chemical exchange would be faster. The isotopic composition of the SiF₄ was checked by an infrared analysis which gave 28±2 percent Si²⁸F₄.

Figure 1 suggests an amusing and direct way to set an experimental maximum for the gyomagnetic ratio of Si²⁸. The splitting in gauss of the fluorine resonance in Si⁴F₄ is given as[4] $\delta H = C\gamma \times (\text{Si}^4)/\hbar$, where C is a constant determined by the electronic structure of SiF₄. The central component in Fig. 1 is from the Si²⁸F₄ and splitting of it greater than 2 milligauss would be discernible. If we take the ratio of the equations for the splitting in Si²⁸F₄ and Si²⁹F₄, introduce the values of 2 and 46 milligauss for the splitting and the experimental value[1] for $\gamma(\text{Si}^{29})$, we find $\gamma(\text{Si}^{28}) < 0.05$. This value could be improved by taking greater pains to obtain maximum resolution and to minimize the effects of chemical exchange. Similar experiments are feasible in several other cases, including C¹²H₄ − C¹³H₄ and H₂S³² − H₂S³³ mixtures.

[1] H. E. Weaver, Phys. Rev. 89, 923 (1953).
[2] R. H. Sands and G. E. Pake, Phys. Rev. 89, 896 (1953).
[3] R. L. White and C. H. Townes, Phys. Rev. 92, 1256 (1953).
[4] Gutowsky, McCall, and Slichter, J. Chem. Phys. 21, 279 (1953).
[5] C. J. Hoffman and H. S. Gutowsky, Inorg. Syntheses 4, 145 (1953).
[6] Gutowsky, Meyer, and McClure, Rev. Sci. Instr. 24, 644 (1953).
[7] H. S. Gutowsky and A. Saika, J. Chem. Phys. 21, 1688 (1953).

Fig. 1. The F¹⁹ nuclear magnetic resonance in a mixture of Si²⁸F₄ and Si²⁹F₄. The center line is from the Si²⁸F₄. The two outer lines are from the Si²⁹F₄; their separation is 46 milligauss. A sawtooth sweep of 135 milligauss was used; the pip on the far right is from the return trace.

Structural Investigations by Means of Nuclear Magnetism. III. Ammonium Halides*

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The proton magnetic resonance absorption has been measured in NH_4Cl, NH_4Br, and NH_4I crystal powders from $-195°C$ to room temperature, and for NH_4Cl to $200°C$. Line width transitions were found at -144, -171, and about $-198°C$ in the chloride, bromide, and iodide, respectively. The $N-H$ distance in the ammonium ion was determined to be $1.035\pm0.01A$ from the second moments of the broad, low-temperature absorption lines observed in NH_4Cl and NH_4Br, with allowance for broadening by modulation effects and narrowing by zero-point torsional oscillations. The relatively narrow room temperature line shapes are consistent with the broadening estimated for inter-NH_4^+ interactions, the intra-NH_4^+ interactions averaging to zero over the hindered rotational motions of the NH_4^+ ions. No appreciable line shape changes were found at the λ temperatures. An electrostatic calculation is made of the potential barriers to rotation of the NH_4^+ ion giving values comparing favorably with experimental inferences. The results clarify the motions which narrow the absorption line at low temperatures and emphasize the dynamic aspects of the order-disorder process.

1. INTRODUCTION

IN papers I[1] and II[2] methods were presented by means of which nuclear magnetic resonance absorption line shapes, widths, and second moments can give information about internuclear distances and motions in solids. In I a brief analysis was made of the broad proton resonance in several ammonium halides at low temperatures, giving a value of 1.025A for the $N-H$ distance in the ammonium ion. At higher temperatures, the proton resonance lines in ammonium salts are narrower, suggesting[3] low-frequency rotational motions of the ammonium ions. This article includes detailed experimental results on polycrystalline ammonium halides, at temperatures of $-195°C$ and higher. The determination of the $N-H$ distance in the ammonium ion is treated more exactly, and the motions responsible for narrowing the resonance lines are considered. In addition, the article[4] following this one gives results obtained with a single crystal of ammonium chloride, for which a more complete analysis and more comprehensive conclusions are possible.

Since the discovery by Simon[5] in 1922 of the anomaly in the specific heat of ammonium chloride at $-30.4°C$, an enormous amount of experimental data and theoretical discussion has been published on the properties and nature of this and similar transitions in other ammonium salts. The infrared spectra of several of the ammonium halides,[6,7] as well as the analysis by Lawson[8] of the specific heat, indicate strongly that the room temperature modifications contain NH_4^+ tetrahedra which are randomly oriented in the two possible equilibrium positions in the unit cells, with the hydrogen atoms directed essentially toward four of the surrounding eight halide ions at the unit cube corners. In the low-temperature phase, the NH_4^+ orientations are ordered, suggesting that the transitions are of an order-disorder type. Conclusive confirmation of this model has since been provided by the more direct neutron diffraction studies[9,10] of the structures of the hydrogen and deutero-ammonium chlorides and bromides. However, the details of the order-disorder process are still not understood, and in particular interesting questions remain concerning the motion of the ions.

Prior to our earlier nuclear resonance studies of the ammonium salts, qualitative observations on NH_4Cl were made by Bitter[11] and by Alpert.[12] Since then, Sachs and Turner[13] have measured proton spin-lattice relaxation times in NH_4Cl, NH_4Br, NH_4I, and NH_4IO_3 from -195 to $25°C$. Soutif[14] has reported line width *versus* temperature data on a single crystal of NH_4Cl, and Cooke and Drain[15] have made some line width and relaxation time observations on NH_4Cl, NH_4Br, and

* Supported in part by the U. S. Office of Naval Research.
[1] Gutowsky, Kistiakowsky, Pake, and Purcell, J. Chem. Phys. 17, 972 (1949).
[2] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. 18, 162 (1950).
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[13] The results are summarized by E. M. Purcell, Physica 17, 282 (1951); details are given by A. M. Sachs, Ph.D. thesis, Harvard University, 1949.
[14] M. Soutif, Rev. sci. 89, 203 (1951).
[15] A. H. Cooke and L. E. Drain, Proc. Phys. Soc. (London) A65, 894 (1952).

NH$_4$I. The results generally agreed upon can be summarized as follows. For each ammonium salt there is a characteristic temperature range above which the resonance absorption line is relatively narrow and structureless and below which the line is very broad with unresolved fine structure. The resonance absorption does not change significantly at the λ temperatures. The width of the broad proton resonance arises from the magnetic dipole-dipole interaction of a given proton with the other three protons in the same NH$_4^+$ ion and also with all other neighboring magnetic nuclei in the crystal. A conclusion supported by the present work is that the narrowing of the line marks the disappearance of the intra-NH$_4^+$ interactions and a slight modification of the smaller, inter-ionic interactions. The disappearance of the intra-NH$_4^+$ interactions results from random reorientations of the NH$_4^+$ ions at an average frequency comparable to the inverse, proton spin-spin interaction time ($\sim$10^5 cps).

This frequency is much too low to contribute appreciably to the specific heat or most of the other physical observables, and one main advantage of nuclear magnetic resonance is that the presence of such low-frequency processes can be detected. The measurements raise the problem of interpreting the low-frequency motions in terms of the crystalline potential
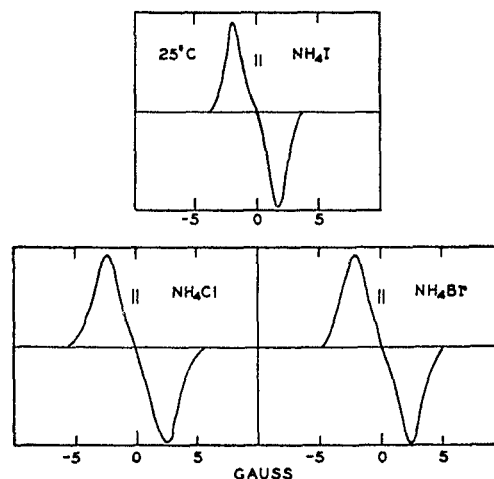
FIG. 2. Derivatives of the proton magnetic resonance absorption lines observed in the ammonium halide powders at room temperature. The absorption intensities are arbitrary. The pairs of vertical lines represent the field modulation.

barriers. The barriers are calculated electrostatically with results comparing favorably with the values deduced from the observed torsional frequencies.[6] The electrostatic calculations, relaxation times, and line shape studies combine to give a physically reasonable dynamical model for the rotational motions of the NH$_4^+$ ions and for the order-disorder process.

2. EXPERIMENTAL METHOD

The data reported here were obtained with the automatic recording rf spectrometer and cryostat described elsewhere.[16] In general, these observations agree with the earlier ones,[1,3] the main differences arising from more effective temperature control in the present arrangement. A fixed radio-frequency of about 27.2 mc was used. The applied magnetic field was modulated a small fraction of the line width, and the derivative of the proton resonance line was plotted automatically as a function of applied field by a recording potentiometer, preceeded by a narrow-band amplifier.

The samples were polycrystalline, reagent grade, from commercial sources. An arbor press was used to make cylindrical pellets $\frac{3}{8}$ inch in diameter and $\frac{3}{4}$ inch long. The temperature was measured with a copper-constantan thermocouple imbedded in a small hole drilled in one end of the pellet. Complete line shapes were obtained at fixed temperatures over the temperature range investigated. There were significant differences in the line shapes observed upon warming and cooling through the line-width transition region. The differences could arise from a lag in attaining temperature equilibrium, most likely from the less effective temperature control upon cooling; however, there might be a true hysteresis. In any event, all data re-
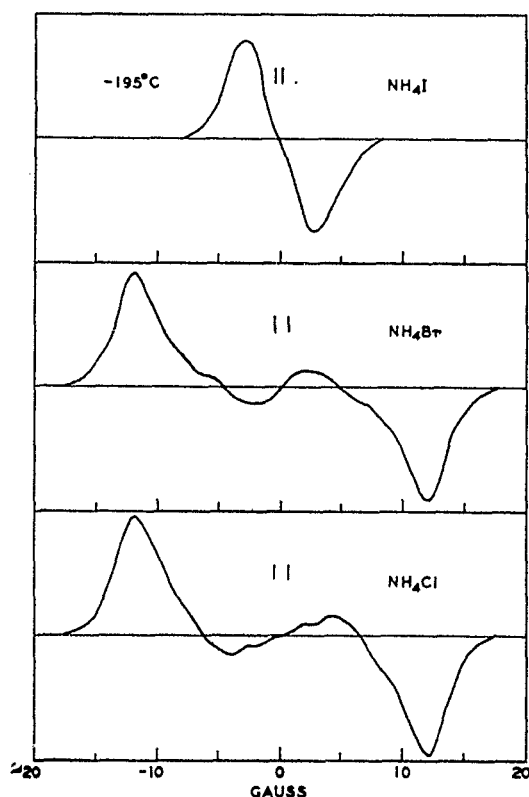

FIG. 1. Derivatives of the proton magnetic resonance absorption lines observed in the ammonium halide powders at liquid nitrogen temperatures. The absorption intensities are arbitrary. The pairs of vertical lines represent the field modulation.

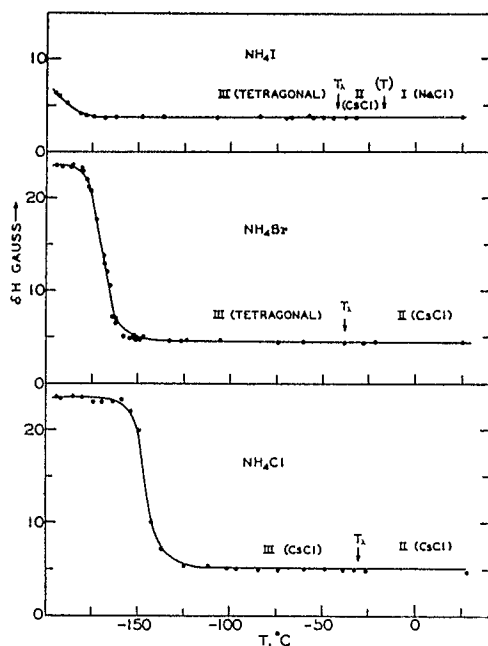[16] Gutowsky, Meyer, and McClure, Rev. Sci. Instr. 24, 644 (1953).

FIG. 3. Line widths of the proton magnetic resonance absorption in the ammonium halide powders plotted against temperature. The curves drawn for NH_4Cl and NH_4Br were calculated from T_1 results as described in Sec. 3c.

ported in the line-width transition region were obtained upon warming.

Second moments of the absorption lines were obtained by numerically integrating the observed first derivatives. The errors given in the text for second moments are the statistical errors of the observations. In addition, nonlinearity and systematic error in the biasing current-field change calibration introduce a further uncertainty of no more than one percent of the observed second moment values. *Both* errors are taken into consideration in calculating the N—H bond distance. The experimental errors in the line widths depend somewhat on the line shape; usually the statistical and maximum systematic errors together were no more than two percent of the values reported.

3. RESULTS AND DISCUSSION

The absorption line shapes observed at liquid nitrogen temperature are given in Fig. 1 and those at room temperature in Fig. 2. The line widths δH, defined as the separation in gauss between the maximum and minimum of the derivative of the absorption line, are plotted against temperature in Fig. 3; also included are the various phases of the ammonium salts and their transition temperatures. Second moments ΔH_2^2, obtained from some of the better observed derivatives, are plotted against temperature in Fig. 4. With the exception of the room temperature and liquid nitrogen temperature data, the points in Figs. 3 and 4 usually represent single observations. The line widths and second moments given in Table I for those two temperatures

are averages of at least three different plotted line shapes. Ammonium fluoride is not included in this report as its structure differs significantly from that of the other halides.

a. Low Temperature Line Shapes and the N—H Distance in the Ammonium Ion

Figure 4 shows that the second moments in the chloride, and probably the bromide as well, have reached limiting values at $-195°C$. These values no doubt correspond to "rigid lattices" and can be used to evaluate the N—H distance in the ammonium ion. Van Vleck's theoretical result[17] for the second moment may be written for the proton resonance in the ammonium halides as[1]

$$\Delta H_2^2 = (9/32)g^2\beta^2\{ \sum_{i<i'} (3\cos^2\theta_{jj'}-1)^2 r_{jj'}{}^{-6}$$
$$+ (1/2) \sum_{j,k} (3\cos^2\theta_{jk}-1)^2 r_{jk}{}^{-6}\}$$
$$+ (1/12)I_f(I_f+1)g_f^2\beta^2 \sum_{i,f}(3\cos^2\theta_{jf}-1)^2 r_{jf}{}^{-6}; \quad (1)$$

g is the proton gyromagnetic ratio; β is the nuclear magneton; the indices j and j' refer to the four protons
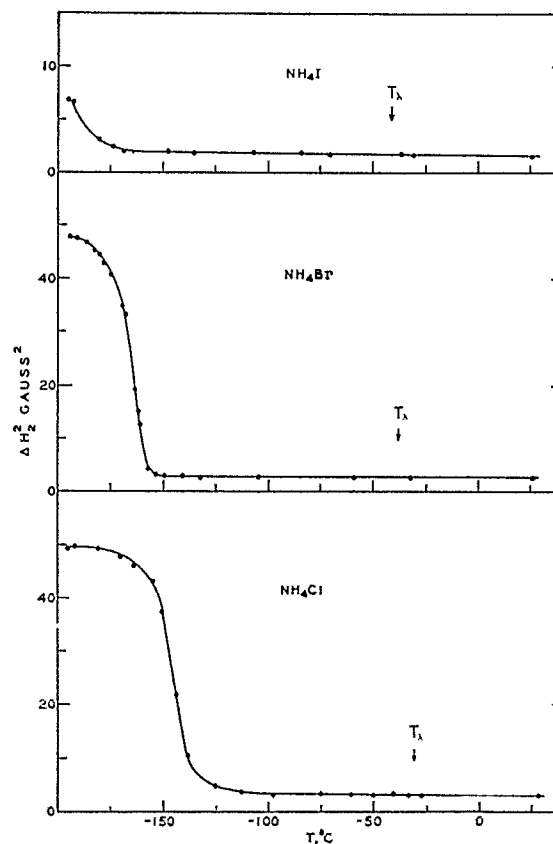

FIG. 4. Second moments of the proton magnetic resonance absorption in the ammonium halide powders plotted against temperature.

[17] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

TABLE I. Proton absorption line widths and second moments observed for the ammonium
halide powders at −195°C and 25°C.

Compound	Line width, δH		Second moment, ΔH_2^2		N−H distance
	25°C	−195°C	25°C	−195°C	
NH₄Cl	4.8 gauss	23.4 gauss	3.35±0.05 gauss²	49.5±0.5 gauss²	1.038±0.004A
NH₄Br	4.6	23.7	2.70±0.03	48.0±0.5	1.031±0.004
NH₄I	3.8	5.9	1.55±0.02	6.85±0.2	

in a given NH_4^+, k to all other protons and f to all other magnetic nuclei in the sample; r_{jk} is an internuclear distance and θ_{jk} is the angle between $\mathbf{r}_{jk}$ and the applied magnetic field. If the crystal structure is known except for the N−H distance r, Eq. (1) is essentially a one-parameter equation, and r can be computed from it and the observed second moment. In the earlier calculation[1] two factors were neglected: (a) the possible broadening of the experimental absorption line by the field modulation; and (b) the effect of zero-point torsional vibrations of the ammonium ion in the calculation of the theoretical second moment. It turns out that the two effects nearly cancel, giving corrected values for the N−H distance agreeing with the original results.[1]

Relatively large modulation amplitudes were used initially. Perlman and Bloom[18] showed by an approximate method that this introduces an appreciable error in the second moments. Andrew[19] has given a direct calculation of the effect, obtaining the true second moment by subtracting $h_m^2/4$ from the observed, while the Perlman and Bloom correction is $h_m^2/3$. h_m is the modulation amplitude, i.e., one-half the values shown in Figs. 1 and 2. An experimental check was made of the correction by plotting the room temperature proton resonance in ammonium bromide as a function of modulation amplitude, at amplitudes less than the line width. The resultant second moments, which are averages of several plots at the two smallest modulations, are plotted against h_m in Fig. 5, and, for comparison, curves are given corresponding to $h_m^2/4$ and $h_m^2/3$. It is seen that the data are in better agreement with the $h_m^2/4$ correction term. It is of interest to note that the line width δH was 4.6 gauss independent of h_m, even at the maximum $2h_m$ of 3.35 gauss. The second moments reported here and in the following article as well have either been corrected for the modulation or else the modulation amplitude was small enough that the correction is well within the other experimental errors.

The correction for the zero-point torsional vibration is obtained by averaging the angular dependence in Eq. (1) over the motion, instead of assuming a completely rigid lattice and averaging only over the random crystalline orientations. By the spherical harmonic

addition theorem, we can write

$$\langle 3 \cos^2\theta_{jk} - 1 \rangle_{\text{torsional motion}}$$

$$= (3 \cos^2\theta_{jk}{}^0 - 1)\langle \tfrac{1}{2}(3 \cos^2\theta - 1)\rangle, \quad (2)$$

where $\theta_{jk}{}^0$ is the equilibrium value of θ_{jk} and θ is the angle between $\mathbf{r}_{jk}$ and its equilibrium position. θ is appreciable only for the intra-NH_4^+ interactions; and as the ammonium ion behaves like an isotropic oscillator (see Sec. 3d), we find

$$\langle \tfrac{1}{2}(3 \cos^2\theta - 1)\rangle = \langle 1 - \tfrac{3}{2}\theta^2 + \cdots \rangle = 1 - \frac{3h}{8\pi^2 c I \nu}, \quad (3)$$

where I is the moment of inertia of the ion and ν is the torsional frequency in cm^{-1}. The correction factor $(1 - \epsilon)$ is the square of Eq. (3) and introducing it into Eq. (1), averaging over the crystal powder and simplifying, there results

$$\Delta H_2^2 = \left\{ \frac{5832}{81\,920} g^2 + \frac{8}{15} g_N^2 \right\} \beta^2 r^{-6} (1 - \epsilon)$$

$$+ \frac{9}{80} g^2 \beta^2 \sum_{j,k} r_{jk}^{-6} + \frac{1}{15} I_f (I_f + 1) g_f^2 \beta^2 \sum_{j,f} r_{jf}^{-6}. \quad (4)$$

The first term is the intra-NH_4^+ broadening; the second gives the interactions between protons in neighboring
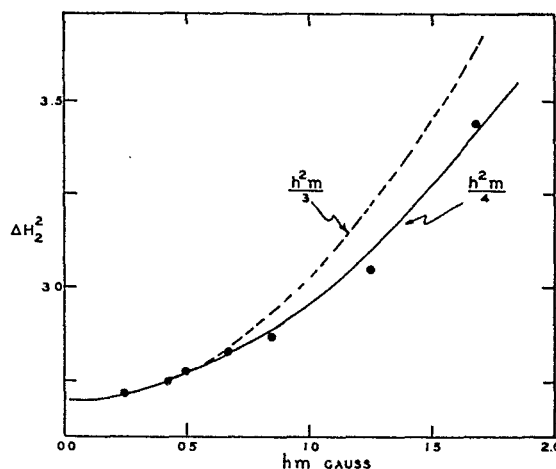
FIG. 5. The second moment of the proton magnetic resonance absorption in NH₄Br powder at room temperature plotted against modulation amplitude h_m. The limiting value at zero modulation is 2.70 gauss². The solid and dotted lines are theoretical values obtained by adding $h_m^2/4$ and $h_m^2/3$, respectively, to 2.70.

[18] M. M. Perlman and M. Bloom, Phys. Rev. 88, 1290 (1952). We wish to thank Mr. Bloom who, prior to publication of their results, pointed out to us the importance of this correction in our original data.
[19] E. R. Andrew, Phys. Rev. 91, 425 (1953).

NH_4^+, and the last represents the effects of the halogen and nitrogen nuclei external to the given NH_4^+.

For NH_4Cl, the second term in Eq. (4) was found to be approximately 6.5 gauss^2 by calculating correctly the interactions of an NH_4^+ with its thirty two nearest neighbors and replacing the remaining ions by points on a simple cubic lattice. The NH_4^+ ions were assumed ordered a-a-a-a; an ordering a-b-a-b; where b is the inverted configuration of a, would give values about 5 percent higher. The results depend on r, which was taken to be 1.04A, and on the size of the CsCl-type unit cell, which has been reported[20] to be 3.820A at $-195°C$. The last term in Eq. (4) is 0.1 gauss^2 for NH_4Cl, determined by computing the actual distances to the nearest eight chlorine and six nitrogen nuclei, replacing the remaining nuclei by points on CsCl and simple cubic lattices, respectively, and using partial summations readily obtained from the total summations given elsewhere.[21] The torsional oscillation frequency of NH_4^+ has been reported[6] to be 390 cm^{-1} in the chloride. With an r of 1.04A, the moment of inertia of NH_4^+ is 4.826 $\times 10^{-40}$ g cm^2. These values in Eq. (3) give 0.913 for $(1-\epsilon)$. As a final result, the observed second moment of 49.5±0.5 gauss^2 leads to a value of 1.038±0.004A for the $N-H$ distance.

For NH_4Br, the calculation of the inter-NH_4^+ broadening is complicated by the tetragonal structure[9] at low temperatures. However, the distortion from a CsCl structure is slight, and the distances are such that only small errors are introduced by assuming the CsCl structure, for which the arithmetic is much simpler. A CsCl lattice constant of 4.11A was adopted, the average of $c+a/(2)^{\frac{1}{2}}$ as reported[9] for $-145°C$. The ordering of the NH_4^+ ions appears[9] to be such that they are parallel along a given c axis of the tetragonal structure, with those along adjacent axes oppositely oriented. This corresponds to an ordering a-b-a-b in the CsCl lattice used. The large lattice constant for NH_4Br permitted the proton-proton distance summations to be approximated by points on a simple cubic lattice after calculations to the six nearest NH_4^+. Otherwise the computations were analogous to those for NH_4Cl. The inter-NH_4^+ broadening was found[22] to be 3.9 gauss^2 and the broadening by bromine and nitrogen nuclei outside the given NH_4^+, 0.4 gauss.^{2} The NH_4^+ torsional frequency is reported[6] as 319 cm^{-1}, giving a value for $(1-\epsilon)$ of 0.894. Combining these results with the observed second moment of 48.0±0.5 gauss^2 yields a value of 1.031±0.004 for the $N-H$ distance.

The 1.038±0.004A value for the $N-H$ distance in NH_4Cl powder is within experimental error of the values 1.031±0.007A and 1.033±0.004A from the

(1,0,0) and (1,1,0) single crystal orientations.[4] The 1.031±0.004A value from NH_4Br powder appears to be identical with those from NH_4Cl. These proton magnetic resonance values are to be compared with the neutron diffraction results[9] of 1.03±0.02A for both ND_4Cl and NH_4Cl and for ND_4Br. Bernal[23] has implied that a change in environment of the NH_4^+ ions might produce a change in bond length. However, any such effect is small, even in NH_4Br where the tetragonal structure suggests the importance of Br^--proton attractions.

b. Resonance Absorption at Temperatures Above the Line-Width Transitions

The relatively narrow absorption lines shown in Fig. 2 persist without significant change from the line-width transitions in the neighborhood of $-150°C$ to room temperature and higher. If the motions of the NH_4^+ ions associated with the line-width transition were restricted to reorientations about a single specific axis, such as a C_2 or C_3 symmetry axis, the intra-NH_4^+ broadening would still be an appreciable fraction^2 of the "rigid-lattice" value. Moreover, for the NH_4Cl single crystal[4] the angular dependence and magnitude of the room temperature second moments are given satisfactorily by a model in which the intra-NH_4^+ broadening is averaged to zero by reorientations effectively about all three of the C_2 axes. The observed line broadening is mainly from inter-NH_4^+ interactions which are reduced only partially by the reorientations, with a small contribution from proton-halogen interactions. This model predicts a value of about 3.40 gauss^2 for NH_4Cl powder, with disordered orientations of the NH_4^+ ions; the observed second moment is 3.35±0.05 gauss^2.

A similar model also appears reasonable for NH_4Br and NH_4I. The distance between NH_4^+ ions is large compared to the $N-H$ distance so the numerical values for NH_4Cl given in Eq. (8) and Table VIII of the following article[4] should yield good approximations for the other halides simply by using their unit cell dimensions. In this manner the inter-NH_4^+ broadening from NH_4Br with a unit cell[9] of 4.060A is 2.50 gauss^2. The observed room temperature second moment is 2.69±0.05 gauss^2 which compares very well with the calculated value when consideration is given to the proton-bromine broadening of 0.4 gauss^2 in the rigid lattice. The case of NH_4I is somewhat different in that the CsCl phase is stable only between -17.6 and $-41.6°C$, with a unit cell of[24] 4.37A. Using the same procedure as for NH_4Br, an inter-NH_4^+ broadening of 1.58 gauss^2 was estimated. This is to be compared with a second moment of 1.75 ±0.05 gauss^2 observed at $-35°C$, with allowance for proton-iodine broadening which is about 0.5 gauss^2 in the rigid lattice.

Once the intra-NH_4^+ broadening disappears, the

[20] L. Vegard and S. Hillesund, Anhandl. Norske Videnskaps-Akad. Oslo. I. Mat-Naturv. Kl. No. 8 (1942); Chem. Zentr. I, 930 (1943).
[21] H. S. Gutowsky and B. R. McGarvey, J. Phys. Chem. 20, 1472 (1952).
[22] These values are somewhat smaller than those given in I, which were based on a smaller lattice constant 4.03A.

[23] M. J. M. Bernal, Proc. Phys. Soc. (London) A66, 514 (1953).
[24] A. Smits and D. Tollenaar, Z. physik. Chem. B52, 222 (1942).

theoretical second moments for the crystal powders are insensitive to the state of motion or ordering of the NH_4^+ ions; and even in a single crystal the angular dependence of the line shape is only slightly different for spherical rotation, and for disordered and ordered reorientations.[4] In agreement with this prediction, the second moments observed for NH_4Cl powder are constant[25] between 3.35 and 3.40 gauss^2 from room temperature to above 150°C. However, NH_4Cl undergoes a phase transition from a CsCl to a NaCl lattice at 184.3°C, and about this temperature the second moment is definitely smaller, for instance, 2.75 gauss^2 at 186.5°C. Detailed calculations were not made for the NaCl lattice, but the observed decrease is qualitatively consistent with the change in lattice structure and dimensions. In the case of NH_4I, the transition between the CsCl and NaCl structures occurs at −17.6°C. The second moment in the NaCl phase at room temperature is 1.55 gauss^2 which is also smaller than the value found in the CsCl phase, 1.75 gauss^2 at −35°C. Cooke and Drain[16] have mentioned a line width change from 4.5 to 5.8 gauss at −17.6°C, which we did not observe although the second moment changed as indicated. However, there is some possibility that the NaCl phase supercooled in our experiments.

From these results we conclude that the intra-NH_4^+ interactions become averaged out during the line-width transition and remain so at higher temperatures. This requires that the reorientations of the NH_4^+ ions, at temperatures above the line-width transitions, do not remain correlated with any specific axis of rotation for times greater than about 10^{-4} sec. Accordingly, some modification is required in the model postulating[26] one dimensional rotation of the NH_4^+ ions in the NaCl phase of NH_4I, on the basis of the infrared spectrum. Rotation of the NH_4^+ ion can occur about one of its C_3 axes, but there must be interchange in the orientation of the axis about which the rotation occurs. The relatively low interchange frequency required would not affect the infrared spectrum or heat capacity. Three models for the NaCl phase of ND_4Br and ND_4I were

TABLE II. Frequency factors and activation energies for reorientations of the NH_4^+ ion.

Compound	T_1 measurements[a] $(\tau_c)_0$	E	Line-width transitions T_t[b]	E
NH_4Cl	2.6×10^{-14} sec	4740 cal	−144.1°C	4740[c] cal
NH_4Br	2.0×10^{-13}	3280	−170.6	3340
NH_4I	1.3×10^{-13}	2900	−198.1[d]	2550

[a] These values are from Sachs, reference 13, $\nu_0 = 1/2\pi(\tau_c)_0$.
[b] At this temperature the line width is half way between the limiting values.
[c] Assumed in calculating E values for NH_4Br and NH_4I.
[d] This value was extrapolated by assuming the line-width transition for NH_4I to be of the same general shape as for NH_4Cl and NH_4Br.

[25] In addition to the main resonance, with a width of 4.8 gauss, several samples exhibited a narrow central line gradually increasing in intensity at temperatures above about 50°C; the sharp line was found to originate in adsorbed moisture which could catalyze narrowing by self-diffusion.
[26] R. C. Plumb and D. F. Hornig, J. Chem. Phys. 21, 366 (1952).

found satisfactory by Levy and Peterson[9] in their neutron diffraction studies; of these the single approach model appears to be the only one consistent with all the available evidence.

c. The Line-Width Transitions

The narrowing of the absorption line depends upon the correlation frequency ν_c, the average reorientation rate of the NH_4^+ ions. In the case of a change from a broad line to a narrower line,[2] the frequency width of the line $\delta\nu$ is given as a function of ν_c by the equation

$$(\delta\nu)^2 = B^2 + C^2(2/\pi)\tan^{-1}[\alpha(\delta\nu/\nu_c)]; \qquad (5)$$

where B is the width of the narrow line, $(B^2+C^2)^{\frac{1}{2}}$ is the width of the broad line, and α is a parameter depending upon the line shape with the value unity for a Gaussian shape. The reorientations are presumably thermally activated so the variation with temperature of ν_c is of the form

$$\nu_c = \nu_0 e^{-E/RT}, \qquad (6)$$

which when combined with Eq. (5) should describe the line-width transition. In principle Eqs. (5) and (6) can be combined with the observed line widths to compute E, the activation energy required for reorientation, and ν_0, the frequency factor. However, α is also unknown, complicating the analysis, so a simpler approach is followed.

It is physically reasonable that the NH_4^+ reorientations should be the most effective spin-lattice relaxation process. Sachs[13] and also Cooke and Drain[15] have observed the temperature dependence of the spin-lattice relaxation time T_1 and thereby evaluated E in the different ammonium halides, and also ν_0. The results are summarized in Table II. These E and ν_0 values can be used to compute ν_c values in Eq. (6), and the results, substituted in Eq. (5), should reproduce the line-width transition. The line shape parameter α was evaluated by fitting Eq. (6) to the T, $\delta\nu$, and ν_c values at the center of the transition, giving 4.88 and 10.4 for NH_4Cl and NH_4Br, respectively. In this manner, the lines drawn in Fig. 3 were computed for these compounds. The fit is generally quite good; the deviations for NH_4Br at the ends of the transition are outside experimental error. However, the line shapes change during the transition, (compare Figs. 1 and 2), and this may change α from the assumed constant value. In view of this uncertainty the agreement is as good as one might expect and is surely adequate to demonstrate that the NH_4^+ reorientations determine T_1, as well as the line widths in the transition region.

Wert and Marx[27] have described a procedure which can be adapted to give activation energies for reorientation from the line-width transition temperatures T_t. The correlation frequencies ν_c should be very nearly the same at the line width transition in the different

[27] C. Wert and J. Marx, Acta Metallurgica 1, 113 (1953).

halides, and also the frequency factors ν_0 are only slightly different. Accordingly, Eq. (6) may be written as $E = AT_t$ where the constant A equals $R \ln(\nu_0/\nu)$ and can be evaluated from a known E and T_t. The E value for NH_4Cl of 4740 cal mole^{-1}, from T_1 data, combined with the observed T_t of 129°K, gives a value for A of 36.8 cal deg^{-1}. On this basis the transition temperatures of 102.5 and 75°K for NH_4Br and NH_4I give activation energies of 3340 and 2550 calories. Small corrections have been made for the differences in ν_0, using the T_1 results; if the infrared torsional frequencies are used for ν_0, the results are not affected significantly. The value for NH_4I from the transition temperature is a bit lower than the 2900 calories obtained by Sachs from T_1; however, Cooke and Drain suggest from their T_1 data an approximate, lower value of 1700 to 2200 calories.

The two interpretations given above depend more or less upon the T_1 results. A completely independent evaluation of E could be based upon the second moments observed as a function of temperature, which would eliminate the uncertainties associated with the line shape parameter α. This is touched upon indirectly in a discussion given in the following paper.[4]

d. The Motion of the Ammonium Ion

The experimental evidence presented and reviewed above demonstrates the existence of hindered rotational motion of the ammonium ions. In this section a phenomenological treatment is given which clarifies the nature of the rotational motion.

A phenomenological potential for the ammonium ion can be obtained following a method of Nagamiya.[28] The ammonium ion is assumed electrically to be a system of four point charges of $+e/4$ at the vertices of a rigid, regular tetrahedron. The potential energy of each proton, at a point (x_i, y_i, z_i) in a CsCl-type lattice, with respect to all charges outside of its own ion, is

$$V = \frac{1}{d}\left\{ c_0 + c_4\left(\frac{r}{d}\right)^4\left(\frac{x_i^4 + y_i^4 + z_i^4}{4} - \frac{3}{5}\right) + \cdots \right\}, \quad (7)$$

where d is the unit cell size and r is the N—H distance, taken to be 1.04A. The first term is very much larger than the second, but the second has an angular dependence which is the chief hindrance to rotation of the ammonium ion. Therefore, a suitable potential for the rotation is

$$V = \frac{V_0}{2}\sum_{i=1}^{4}\left(\frac{x_i^4 + y_i^4 + z_i^4}{r^4} - \frac{3}{5}\right). \quad (8)$$

For the specific model of the ion proposed above

$$V_0 = \frac{35}{36}\left(\frac{e}{4}\right)^2\sum_j\frac{(\pm 1)}{r_j^5} = 46.8\left(\frac{e}{4}\right)^2\frac{r^4}{d^5}, \quad (9)$$

[28] T. Nagamiya, Proc. Phys. Math. Soc. Japan 24, 137 (1952).

Compound	ν(obs[a])	V_0 (Eq. 9)	V_0 (Eq. 14)[a]	E_0[b]
NH_4Cl	390 cm^{-1}	5400 cal	5250 cal	6410 cal
NH_4Br	319	3730	4180	4645
NH_4I	279	2910	2850	4100

[a] These values are obtained from the observed torsional frequencies ν, while the V_0 (Eq. 9) results are entirely from an electrostatic calculation.
[b] $E_0 = E$ (from T_1 in Table II) $+ (3/2)h\nu_{obs}$.

where r_j is the distance from a given nitrogen nucleus to a chloride ion or another nitrogen nucleus, the sign being $+$ or $-$ respectively. Values of V_0 computed with Eq. (9) for the different halides are given in Table III.

The potential in Eq. (8) is more general than the particular model used in obtaining Eq. (9). To demonstrate this generality the summation in Eq. (8) is carried out by introducing new coordinates. An x', y', z' system is fixed in the ion such that at equilibrium the z' axis coincides with the z cubic axis, but the x', y' axes are rotated by $\pi/4$ with respect to the x, y cubic axes. θ, ϕ are the polar coordinates of the z' axis and ψ measures rotation of the ion about the z' axis. In terms of these angular coordinates Eq. (8) becomes

$$V = \frac{1}{2}V_0\{-(49/8)\cos^4\theta + (21/4)\cos^2\theta - (21/40)$$
$$+ (7/8)\sin^4\theta\,(\cos4\psi - \cos4\phi)$$
$$+ (\cos^2\theta + \tfrac{1}{8}\sin^4\theta)\cos4\phi\,\cos4\psi$$
$$- \tfrac{1}{2}(\cos\theta + \cos^3\theta)\sin4\phi\,\sin4\psi\}. \quad (10)$$

This is the simplest nontrivial potential having the cubic symmetry of the lattice and the tetrahedral symmetry of the ion. The general solution of the Schrödinger equation for a spherical top moving in such a potential is formidable and we confine ourselves to the limit of small oscillations.[29]

For small, commuting rotations we can choose as coordinates

$$\xi = \theta \cos\phi$$
$$\eta = \theta \sin\phi \quad (11)$$
$$\zeta = \phi + \psi + \pi/4,$$

the angles of rotation about the cubic x, y, z axes. Developing the potential energy in a power series of small rotations about the equilibrium position, we obtain

$$V \cong \frac{V_0}{2}\left\{ -\frac{12}{5} + 8(\xi^2 + \eta^2 + \zeta^2) - \frac{32}{3}(\xi^4 + \eta^4 + \zeta^4)\right.$$
$$\left. - 8(\xi^2\eta^2 + \xi^2\zeta^2 + \eta^2\zeta^2) + \cdots \right\}. \quad (12)$$

Using first-order perturbation theory the energy levels

[29] In so doing we give up the possibility of calculating tunnelling frequencies.

of this anharmonic isotropic oscillator are computed to be

$$E_{n_1 n_2 n_3} = -\frac{6}{5}V_0 + (n_1 + n_2 + n_3 + 3/2)\hbar\omega$$

$$-\frac{1}{16}\left[\sum_{i=1}^{3}(2n_i^2 + 3n_i + 5/4)\right.$$

$$\left. + n_1 n_2 + n_1 n_3 + n_2 n_3\right](\hbar\omega)^2/V_0, \quad (13)$$

where $\hbar\omega = (16V_0(\hbar^2/2I))^{\frac{1}{2}}$ and I is the moment of inertia of the ammonium ion. If ν is the observed torsional frequency, i.e., $h\nu = E_{100} - E_{000}$, then from the energy levels we deduce that

$$V_0 = \frac{1}{16}\frac{(h\nu + 5\hbar^2/2I)^2}{\hbar^2/2I}. \quad (14)$$

The experimental torsional frequencies, from spectral data, are listed in Table III with the corresponding V_0 values calculated using Eq. (14). These experiment based V_0 values agree well with those determined by Eq. (9). So the simple model used in the electrostatic calculation of Eq. (9) gives reasonable results, supporting Pauling's view[30] that the charge on a polyatomic ion is distributed on the surface of the ion.

We turn now to the essential meaning of V_0. If an NH_4^+ ion rotates from one equilibrium configuration to another around a fourfold cubic axis it passes over a barrier of total height V_0. On the other hand, if an ion rotates around a threefold cubic axis (with one proton fixed) the barrier is $(16/9)$ V_0, as may be seen from Eq. (8). The activation energy E, as given by the T_1 and line-width transition analyses, corresponds to the energy, above the ground state, of the NH_4^+ ions in

their reorientations. If the values of E are corrected by adding the zero point torsional energy of the ground state, the total barrier height E_0 is obtained. These experimentally inferred values are listed in Table III; they are larger than V_0 but less than $(16/9)$ V_0 and thus are between the barriers for rotation about a cubic fourfold axis and a cubic threefold axis. Therefore, the motion of the ion which is most important in relaxing the proton spins and in narrowing the absorption line is a motion which classically is partially free and partially hindered. This type of motion accounts for the averaging completely to zero of the intra-NH_4^+ contribution to the line width. Moreover, the experimental values of ν_0 given in Table II are the right order of magnitude for classical rotation frequencies of the ions.

e. The Order-Disorder Process

The preceding results and conclusions emphasize the dynamic nature implicit in the order-disorder process at T_λ, as was pointed out some time ago by Purcell.[13] Even at low temperatures in the ordered phase the ammonium ions experience occasional random reorientations, but return to the stable, ordered configuration. As the temperature is increased, the rate of the reorientations and the fraction of ions reorienting at a given instant increase. The slightly lower energy of the ordered phase results[28] mainly from the electrostatic interactions of neighboring NH_4^+ ions. When too large a fraction of the NH_4^+ ions are in motion, the coherency of these electrostatic interactions and the return of the ions to the ordered configuration break down, producing a cooperative order-disorder process. The over-all motions of the ions are not modified appreciably by the degree of order primarily because a reorienting ion is in a highly excited energy level, while the order-disorder energy is small, i.e., $RT_\lambda \ll E$.

[30] L. Pauling, J. chim. phys. 45, 142 (1948).

Proton Magnetic Resonance in an Ammonium Chloride Single Crystal*†

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(Received November 18, 1953)

The nuclear resonance absorption spectrum has been calculated theoretically for a tetrahedral 4-spin system, with I of $\frac{1}{2}$, for orientations in which the external magnetic field coincides with a two- or three-fold symmetry axis of the tetrahedron or with a tetrahedral edge. Comparison of the theoretical results with the proton resonance observed at $-195°C$ in a single crystal of ammonium chloride demonstrates that the NH_4^+ ion is oriented with the N—H bonds pointed essentially towards corners of the unit cube. An N—H distance of $1.032 \pm 0.005A$ is determined from the low-temperature second moments of the resonance line with the applied magnetic field in the (1,0,0) and (1,1,0) directions. At room temperature, the anisotropy of the resonance results from inter $-NH_4^+$ interactions, with intra $-NH_4^+$ interactions averaged to zero by hindered rotational motions; free rotation of the ammonium ions does not occur. A small *decrease* with temperature of the second moment of the resonance line at the λ-point agrees with the order-disorder model for the transition. The motion of the NH_4^+ ion is discussed.

1. INTRODUCTION

THE preceeding article[1] gives the results of some proton magnetic resonance absorption experiments on ammonium halide crystal powders. However, the data obtained from a crystal powder consist of a single line shape and its second moment. Accordingly, more than one structural parameter can seldom be evaluated from the powder data, in this case the N—H distance in the ammonium ion. But, if a single crystal is available (about 1 cm³), the angular dependence of the resonance absorption provides additional data which permit a much more detailed analysis of the structure of the sample and of the nuclear magnetic dipole interactions themselves. This is exemplified by Pake's study[2] of a gypsum single crystal, and also by some recent research on $K_2HgCl_4 \cdot H_2O$ and $K_2SnCl_4 \cdot H_2O$ single crystals.[3]

In the case of the ammonium halides, the experiments by Soutif[4] and this work are apparently the only magnetic resonance experiments in which single crystals were used. The present work, believed to be more comprehensive than that of Soutif, leads to the following main results: (a) the orientation and size of the NH_4^+ ion are determined with results in complete agreement with those obtained from neutron diffraction;[5] (b) at temperatures for which the line breadth has reached its narrow value, the remaining breadth is due exclusively to interionic broadening. The first conclusion is based upon a theoretical calculation of the absorption spectrum for the tetrahedral 4-proton system in the am-

monium ion and a comparison with the low temperature line shapes and second moments. The second conclusion is obtained by using Van Vleck's procedure[6] to calculate the second moments for several models and comparing the results with the anisotropy observed in the room temperature resonance.

Relatively little direct information is obtained on the order-disorder transition itself.[7] Firstly, an ion in a disordered position differs from an ion in an ordered position only by an inversion; a "disordered" ion therefore has the same discrete spectrum as an "ordered" ion. Secondly, the small interionic interactions are not very sensitive to the degree of order.

2. EXPERIMENTAL METHOD AND RESULTS

The general experimental procedure was identical with that described or referred to in the preceding article. The single crystal on which the reported measurements were made was rectangular in shape, 14 by 14 by 7 mm; it was supplied by Dr. H. A. Levy and Dr. S. W. Peterson. Some preliminary experiments were performed, with similar results, on a smaller crystal very kindly supplied by Mr. Meyer Bloom. The crystal was oriented visually in the applied magnetic field; line shapes were then plotted at several small angular displacements to ascertain the orientation giving the maximum or minimum line width, and this orientation was undisturbed in the record runs. The crystal shape caused some difficulty in orienting the applied magnetic field in the (1,1,1) direction; it was primarily for this reason that line shapes were not obtained as a function of temperature for this orientation, particularly as the other two orientations gave data sufficient for the present purposes.

The observed derivatives of the proton absorption line are given in Figs. 1 and 2 for the applied magnetic

* Assisted by the U. S. Office of Naval Research.
† Presented in part at the Washington Meeting of the American Physical Society, May, 1952; R. Bersohn, Phys. Rev. 87, 226(A) (1952).
[1] Gutowsky, Pake, and Bersohn, J. Phys. Chem. 22, 643 (1954).
[2] G. E. Pake, J. Chem. Phys. 16, 327 (1948).
[3] Itoh, Kusaka, Yamagata, Kiriyama, and Ibamoto, J. Phys. Soc. Japan 8, 293 (1953).
[4] M. Soutif, Rev. sci. 89, 203 (1951).
[5] H. A. Levy and S. W. Peterson, Phys. Rev. 86, 766 (1952); J. Am. Chem. Soc. 75, 1536 (1953).

[6] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).
[7] An erroneous statement to the contrary was made by one of us (R.B.) in the first reference (†) cited.
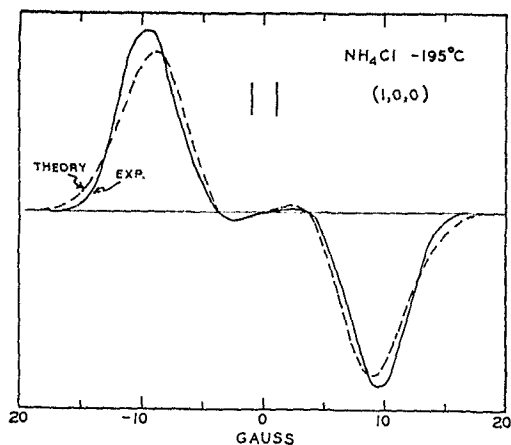
FIG. 1. Derivative of the proton magnetic resonance absorption line in a single crystal of ammonium chloride at −195°C with the magnetic field applied in the (1,0,0) direction. The dashed line is the result of a theoretical calculation described in the text. The vertical pair of lines represents the field modulation.

field in the (1,0,0) and (1,1,0) orientations, respectively, at −195°C, and in Fig. 3 for the (1,0,0), (1,1,0), and (1,1,1) orientations at room temperature. The dashed lines in Figs. 1 and 2 are theoretical line shapes; the details of the comparison are discussed later. The experimental data in Figs. 1 to 3 have been replotted; a direct reproduction of an original recording for the (1,1,0) orientation at −160°C has been given in the article[8] describing the instrumentation. The line widths, defined as the separation in gauss of the maximum and minimum of the derivative, are plotted in Fig. 4 as a function of temperature for the (1,0,0) and (1,1,0) orientations. A similar plot of the second moments, computed numerically from some of the better line
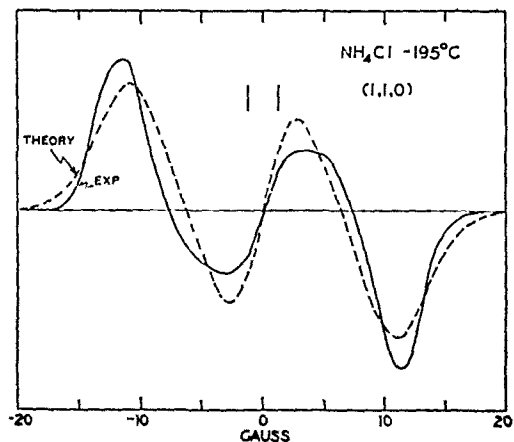

FIG. 2. Derivative of the proton magnetic resonance absorption line in a single crystal of ammonium chloride at −195°C with the magnetic field applied in the (1,1,0) direction. The dashed line is the result of a theoretical calculation described in the text. The vertical pair of lines represents the field modulation.

[8] Gutowsky, Meyer, and McClure, Rev. Sci. Instr. 24, 644 (1953).

shapes, is given in Fig. 5. Table I gives values of the line widths and second moments observed at −195°C, room temperature, and just above and below the λ point, for various orientations of the crystal with respect to the applied magnetic field. These values are averages of at least three separate observations; the experimental errors are discussed in the preceeding article.[1]

3. THEORETICAL COMPUTATION OF THE SPECTRUM OF THE FOUR PROTON SYSTEM

(a) Introduction

The most striking confirmation of the assumed orientation[1] of the ammonium ions comes from examination of the actual line shape. A discrete spectrum for a system of four protons is calculated. The smaller inter-
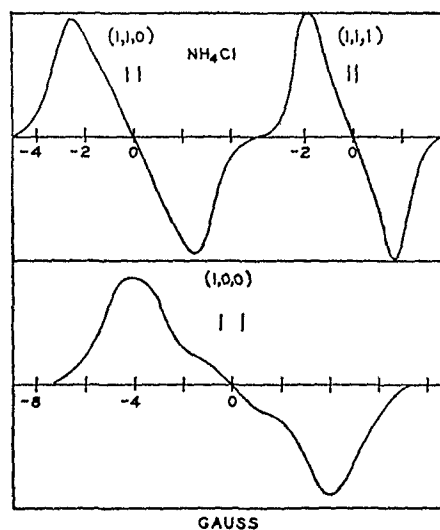

FIG. 3. Derivatives of the proton magnetic resonance absorption line in a single crystal of ammonium chloride at room temperature with the magnetic field applied in the (1,0,0), (1,1,0), and (1,1,1) directions. The vertical pairs of lines represent the field modulation.

actions with other neighboring nuclei are then introduced approximately by smearing the discrete lines so that the second moment agrees with experiment. This procedure is in the spirit of Pake's[2] and Andrew's[9] work on the two- and three-proton systems. Although the resulting line has structure, unlike the two-proton system the structure is unresolved and has qualitative rather than quantitative significance; one cannot use a separation between peaks as a measure of an internuclear distance.

The magnetic Hamiltonian for the four-proton system is

$$\mathcal{H} = -\sum_{i=1}^{4} g\beta H I_{zi} + \sum_{i<j} A_{ij}(\mathbf{I}_i \cdot \mathbf{I}_j - 3I_{iz}I_{jz}), \quad (1)$$
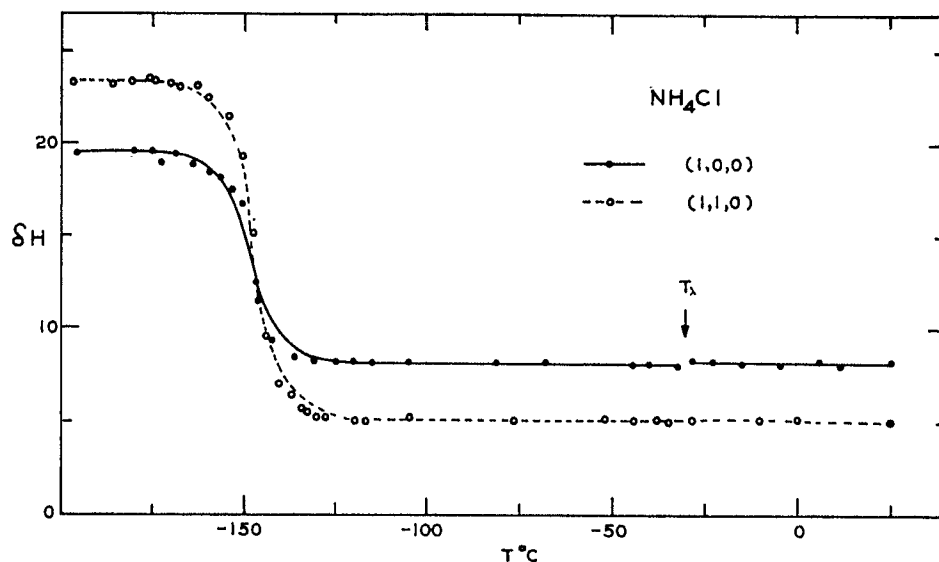
where

$$A_{ij} = g^2\beta^2 r_{ij}^{-3}[(3/2)\cos^2\theta_{ij} - \tfrac{1}{2}],$$

[9] E. R. Andrew and R. Bersohn, J. Chem. Phys. 18, 159 (1950).

FIG. 4. The width of the proton magnetic resonance absorption line in a single crystal of ammonium chloride as a function of temperature with the magnetic field applied in the (1,0,0) and (1,1,0) directions.

and θ_{ij} is the angle between the field $\mathbf{H}$ and $\mathbf{r}_{ij}$, the vector connecting dipoles i and j; g is the proton gyromagnetic ratio and β the nuclear magneton.

Because we are interested only in transitions in which angular momentum components change by $\pm\hbar$, only that part of the dipole-dipole interaction has been included which commutes with the Zeeman energy. If M is the quantum number associated with the z component of the total angular momentum, we expect two singlets $(M=\pm2)$, two quartics $(M=\pm1)$, and a sextic $(M=0)$. Actually the sextic will factor into two cubics if the states are labelled by I, the total angular momentum quantum number. For an arbitrary orientation of the external magnetic field no further factoring is possible.

(b) Conservation Conditions for Factoring the Secular Equation

For the purpose of seeing whether further factoring is possible, a representation is introduced which diagonalizes the squares of the operators

$$\mathbf{L}=\mathbf{I}_1+\mathbf{I}_2, \quad \mathbf{S}=\mathbf{I}_3+\mathbf{I}_4, \quad \text{and} \quad \mathbf{I}=\mathbf{L}+\mathbf{S}.$$

It is appropriate to introduce the quantum number I, because I^2 commutes with all terms of the form $\mathbf{I}_j\cdot\mathbf{I}_k$. The matrix elements for the general case are most easily calculated in an $M_1M_2M_3M_4$ representation which makes necessary the transformation (given in Table II) from the LSIM basis to the $M_1M_2M_3M_4$ basis.

Table III shows the matrix elements of the Hamil-

FIG. 5. The second moment of the proton magnetic resonance absorption line in a single crystal of ammonium chloride as a function of temperature with the magnetic field applied in the (1,0,0) and (1,1,0) directions.
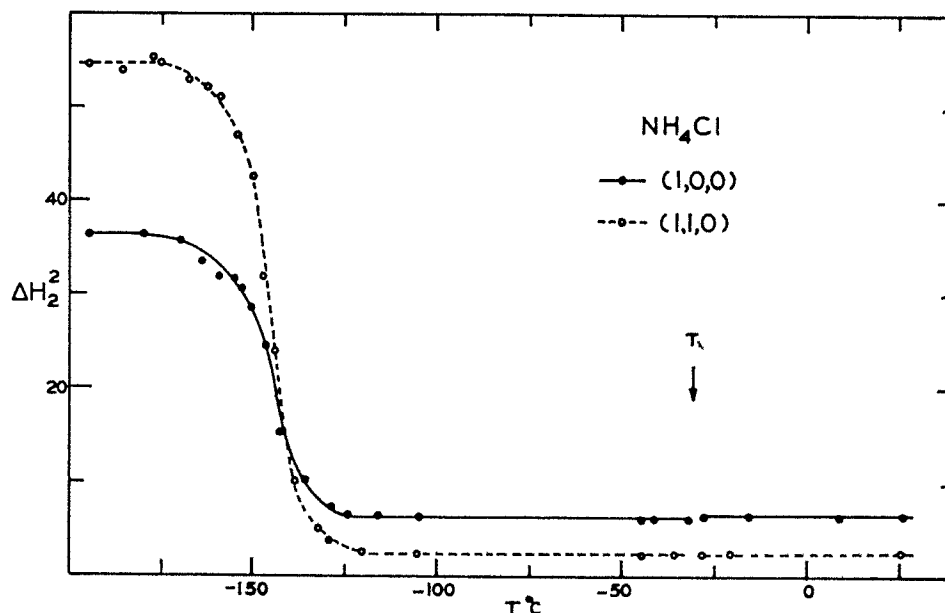
TABLE I. Line widths and second moments observed for the proton magnetic resonance in a single crystal of NH_4Cl at different orientations and temperatures.

Temperature °C	Line width, δH in gauss			Second moment, $\Delta H_2{}^2$ in gauss²		
	(1,0,0)	(1,1,0)	(1,1,1)	(1,0,0)	(1,1,0)	(1,1,1)
25	8.2	5.05	3.55	6.70±0.10	2.63±0.03	1.35±0.02
−28	8.3	5.10	...	6.62±0.15	2.64±0.05	...
−32 to −36	8.05	5.10	...	6.35±0.15	2.57±0.05	...
−195	19.5	23.3	...	36.5±0.7	54.6±0.6	...

tonian in the LSIM representation. Now a conservation law for any set of angular momenta will correspond to the factoring of the secular equations because they are cubic and quartic by virtue of the nonconservation of the angular momentum operator L^2, S^2, and I^2.

The Hamiltonian can be written down in the form of an operator which will commute with the square of a given angular momentum and an operator which will not commute. Sufficient conditions for factoring the secular equation will result from setting the latter operator equal to zero. For example we can write the interaction Hamiltonian in the form

$$\mathcal{H} = A_{12}(\mathbf{I}_1 \cdot \mathbf{I}_2 - 3I_{1z}I_{2z}) + A_{34}(\mathbf{I}_3 \cdot \mathbf{I}_4 - 3I_{3z}I_{4z})$$
$$+ \tfrac{1}{2}(A_{13} + A_{23})[(\mathbf{I}_1 + \mathbf{I}_2) \cdot \mathbf{I}_3 - 3(I_{1z} + I_{2z})I_{3z}]$$
$$+ \tfrac{1}{2}(A_{14} + A_{24})[(\mathbf{I}_1 + \mathbf{I}_2) \cdot \mathbf{I}_4 - 3(I_{1z} + I_{2z})I_{4z}]. \quad (2)$$
$$+ \tfrac{1}{2}(A_{13} - A_{23})[(\mathbf{I}_1 - \mathbf{I}_2) \cdot \mathbf{I}_3 - 3(I_{1z} - I_{2z})I_{3z}]$$
$$+ \tfrac{1}{2}(A_{14} - A_{24})[(\mathbf{I}_1 - \mathbf{I}_2) \cdot \mathbf{I}_4 - 3(I_{1z} - I_{2z})I_{4z}]$$

When $A_{13} = A_{23}$ and $A_{14} = A_{24}$, the Hamiltonian will commute with L^2; and from Table III one can see that the cubics will factor and the quartic will factor into a cubic and a singlet. There are five other equivalent conditions corresponding to the six different ways of choosing a pair of angular momenta. If the tetrahedron is regular, these conditions correspond to having the magnetic filed in one of the six planes of symmetry.

If one asks that L^2 and S^2 be simultaneously conserved, we obtain as necessary conditions

$$A_{13} = A_{14} = A_{23} = A_{24}, \quad (3)$$

with two other equivalent conditions. For a regular tetrahedron, these conditions correspond to having the field along one of the three twofold axes or along one of the six edges. In this case we find

$$\mathcal{H} = A_{12}(\mathbf{I}_1 \cdot \mathbf{I}_2 - 3I_{1z}I_{2z}) + A_{34}(\mathbf{I}_3 \cdot \mathbf{I}_4 - 3I_{3z}I_{4z})$$
$$+ A_{13}(\mathbf{I}_1 + \mathbf{I}_2) \cdot (\mathbf{I}_3 + \mathbf{I}_4) - 3(I_{1z} + I_{2z})(I_{3z} + I_{4z}). \quad (4)$$

If $S^2 = (I_1 + I_2 + I_3)^2$ is to be conserved, then we have

$$A_{12} = A_{13} = A_{23} \quad (5)$$
$$A_{14} = A_{24} = A_{34},$$

with three other equivalent conditions corresponding to orientation of the field along one of the four threefold symmetry axes of a regular tetrahedron.

On inspecting Table III one sees that the conservation conditions in Eq. (3) result in the factoring of the secular equation into quadratics and singlets. Equation (5) is equally effective although it is not obvious in the LSIM representation.

(c) Spectra for Three Orientations of the Magnetic Field

(i) C_3 Orientation

For the C_3 orientation the proper representation is LSIM where $\mathbf{S} = \mathbf{L} + \mathbf{I}_3$. Tomita[10] analyzed the nuclear resonance spectrum of methane by an independent study of the four-spin system. His paper contains the wave functions and Hamiltonian matrix appropriate for the C_3 orientation. Tables IV and V give the energy levels and relative intensity of the ten-line spectrum; in these and subsequent tables, R is the length of the tetrahedral edge.

(ii) C_2 and Edge Orientations

At some expense of complexity in notation the C_2 and edge orientations of the external field can be treated together because they are both cases in which L^2 and S^2 are conserved [condition of Eq. (3)]. The

TABLE II. Transformation from LSIM basis to $M_1M_2M_3M_4$ basis. α_i and β_i are spin functions for an individual nucleus i.

	L	S	I														
ψ_1	1	1	2												$\alpha_1\alpha_2\alpha_3\alpha_4$		$M=2$
$2\psi_2$	1	1	2		1	1	1	1							$\beta_1\alpha_2\alpha_3\alpha_4$		
$2\psi_3$	1	1	1		−1	−1	1	1							$\alpha_1\beta_2\alpha_3\alpha_4$		$M=1$
$\sqrt{2}\psi_4$	1	0	1		0	0	−1	1							$\alpha_1\alpha_2\beta_3\alpha_4$		
$\sqrt{2}\psi_5$	0	1	1		−1	1	0	0							$\alpha_1\alpha_2\alpha_3\beta_4$		
$\sqrt{6}\psi_6$	1	1	2						1	1	1	1	1	1	$\beta_1\beta_2\alpha_3\alpha_4$		
$\sqrt{2}\psi_7$	1	1	1						1	0	0	0	0	−1	$\alpha_1\beta_2\beta_3\alpha_4$		
$2\psi_8$	1	0	1						0	−1	−1	1	1	0	$\beta_1\alpha_2\beta_3\alpha_4$		$M=0$
$2\psi_9$	0	1	1						0	1	−1	−1	1	0	$\beta_1\alpha_2\alpha_3\beta_4$		
$2\psi_{10}$	0	0	0						0	−1	1	−1	1	0	$\alpha_1\beta_2\alpha_3\beta_4$		
$2\sqrt{3}\psi_{11}$	1	1	0						−2	1	1	1	1	−2	$\alpha_1\alpha_2\beta_3\beta_4$		

[10] K. Tomita, Phys. Rev. 89, 429 (1953).

Hamiltonian in Eq. (4) is equivalent to

$$\mathcal{3C} = \tfrac{1}{2}(A_{12}-A_{13})(L^2-3L_z^2)$$
$$+\tfrac{1}{2}(A_{34}-A_{13})(S^2-3S_z^2)+\tfrac{1}{2}A_{13}(I^2-3I_z^2). \quad (6)$$

By means of the matrix[11] $\langle LSIM | LM_L S M_S \rangle$, one can very conveniently calculate the matrix elements and the energy levels with results which are given in Table III and VI, respectively. The spectrum consists of seven lines if the magnetic field is in the C_2 orientation and twenty lines if it is parallel to a tetrahedral edge. The intensities of the lines are given in Table VII. Note that $\sum_{j<k} A_{jk}$ is zero for a regular tetrahedron.

4. ABSORPTION IN NH₄Cl BELOW THE LINE-WIDTH TRANSITION

(a) Comparison of Observed Line Shapes with Calculated Spectra

From the plot in Fig. 5 of second moment *versus* temperature, it is clear that at −195°C the line has reached its broadest possible value. At this temperature motions other than zero-point vibrations are negligible and we will assume that the ammonium ion is a rigid torsional oscillator.

The observed and calculated absorption derivatives at −195°C for the (1,0,0) and (1,1,0) orientations of the magnetic field are shown in Figs. 1 and 2. The calculated derivatives were obtained by replacing each component of the absorption line with the derivative of a Gaussian function whose width corresponded to the broadening computed in Eq. (7) for interactions outside the four-proton system. In order to obtain agreement between the experimental and computed line shapes, it is necessary to assume that the three C_2 axes of the NH₄⁺ tetrahedron are parallel to the cubic axes.

That the agreement is not quite so good for the (1,1,0) curve as the (1,0,0) curve is perhaps to be explained by the smearing approximation used. The (1,1,0) curve consists of 20 separate transitions as compared to the 7 transitions of the (1,0,0) curve. If the different transitions were smeared differently much better agreement could be obtained. It does not seem worth while to pursue this point because NH₄Cl is a poor example to use for this comparison. In most

TABLE III. Matrix elements in LSIM representation.

$$M=2$$

$$\langle 1122|H|1122\rangle = -\tfrac{1}{4}p$$

$$M=1 \text{ (quartic)}$$

diagonal elements

$$\langle 1121|H|1121\rangle = \tfrac{1}{4}p \qquad \langle 1011|H|1011\rangle = -\frac{A_{12}}{2}$$

$$\langle 1111|H|1111\rangle = \tfrac{1}{2}(A_{12}+A_{34})-\tfrac{1}{4}p \quad \langle 0111|H|0111\rangle = -\frac{A_{34}}{2}$$

off-diagonal elements

$$\langle 1121|H|1111\rangle = -\tfrac{3}{4}(A_{12}-A_{34})$$

$$\langle 1121|H|1011\rangle = \frac{3}{4\sqrt{2}}(A_{13}+A_{23}-A_{14}-A_{24}) = 3\langle 1111|H|1011\rangle$$

$$\langle 1121|H|0111\rangle = \frac{3}{4\sqrt{2}}(A_{23}+A_{24}-A_{13}-A_{14}) = -3\langle 1111|H|0111\rangle$$

$$\langle 1011|H|0111\rangle = \tfrac{1}{4}(A_{13}+A_{24}-A_{23}-A_{14})$$

$$M=0$$

$I=0,2$ (cubic)

$$\langle 1120|H|1120\rangle = \tfrac{1}{4}p$$
$$\langle 0000|H|0000\rangle = \langle 1100|H|1100\rangle = 0$$

$$\langle 1120|H|0000\rangle = \frac{\sqrt{6}}{4}(A_{14}+A_{23}-A_{24}-A_{13})$$

$$\langle 1120|H|1100\rangle = \frac{-1}{2\sqrt{2}}(3A_{12}+3A_{34}-p)$$

$$\langle 0000|H|1100\rangle = \frac{\sqrt{3}}{4}(A_{24}-A_{14})$$

$I=1$ (cubic)

$$\langle 0110|H|0110\rangle = A_{34}; \quad \langle 1010|H|1010\rangle = A_{12}$$
$$\langle 1110|H|1110\rangle = \tfrac{1}{2}p - (A_{12}+A_{34})$$

$$\langle 1110|H|1010\rangle = \frac{1}{2\sqrt{2}}(A_{14}+A_{24}-A_{13}-A_{23})$$

$$\langle 1010|H|0110\rangle = \tfrac{1}{2}(A_{14}+A_{23}-A_{13}-A_{24})$$

$$\langle 1110|H|0110\rangle = \frac{1}{2\sqrt{2}}(A_{13}+A_{14}-A_{23}-A_{24})$$

$$p = \sum_{j<k} A_{jk}$$

crystals where the XH₄ or XF₄ groups are further apart the components of the line would be partially resolved.

In the case of solid methane the question has been raised[12] as to whether or not the molecules exist in *ortho* ($I=2$), *meta* ($I=1$), and *para* ($I=0$) states of total proton spin. The nuclear magnetic resonance

TABLE IV. Energy levels when external field is along a C_3 axis.

State in LSIM representation	Energy
$\langle 1\tfrac{3}{2}22 \|$	$2g\beta H$
$I=(\tfrac{1}{2}+\sqrt{7}/4)^{\frac{1}{2}}\langle 1\tfrac{3}{2}21\|+(\tfrac{1}{2}-\sqrt{7}/4)^{\frac{1}{2}}\langle 1\tfrac{3}{2}11\|$	$g\beta H+(\tfrac{1}{4}+\sqrt{7}/2)g^2\beta^2R^{-3}$
$II=(\tfrac{1}{2}-\sqrt{7}/4)^{\frac{1}{2}}\langle 1\tfrac{3}{2}21\|-(\tfrac{1}{2}+\sqrt{7}/4)^{\frac{1}{2}}\langle 1\tfrac{3}{2}11\|$	$g\beta H+(\tfrac{1}{4}-\sqrt{7}/2)g^2\beta^2R^{-3}$
$\langle 1\tfrac{3}{2}11\|, \ \langle 0\tfrac{1}{2}11\|$	$g\beta H-\tfrac{1}{2}g^2\beta^2R^{-3}$
$\langle 1\tfrac{3}{2}20\|, \ \langle 0\tfrac{1}{2}00\|, \ \langle 1\tfrac{1}{2}00\|$	0
$\langle 1\tfrac{3}{2}10\|$	$-g^2\beta^2R^{-3}$
$\langle 1\tfrac{1}{2}10\|, \ \langle 0\tfrac{1}{2}10\|$	$\tfrac{1}{2}g^2\beta^2R^{-3}$

[11] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, reprinted 1951)
[12] T. Nagamiya, Progr. Theoret. Phys. (Japan) 6, 702 (1951).

TABLE V. Intensities of the lines in the C_3 orientation.

$\Delta E = \pm(E_M - E_{M-1} + g\beta H)$	Relative intensity
$\pm(5/4-\sqrt{7}/2)g^2\beta^2R^{-3} = \pm0.073g^2\beta^2R^{-3}$	0.0744
$\pm\frac{3}{4}g^2\beta^2R^{-3}$	0.2500
$\pm(-\frac{1}{4}+\sqrt{7}/2)g^2\beta^2R^{-3} = \pm1.073g^2\beta^2R^{-3}$	0.2534
$\pm(\frac{1}{4}+\sqrt{7}/2)g^2\beta^2R^{-3}\ = \pm1.573g^2\beta^2R^{-3}$	0.3716
$\pm(5/4+\sqrt{7}/2)g^2\beta^2R^{-3} = \pm2.573g^2\beta^2R^{-3}$	0.0506

data for methane,[10] and also for solid hydrogen,[13] are consistent with the existence of nuclear spin isomers. Now the line shape agreement in NH_4Cl depends on the existence of matrix elements between states of different total proton spin, which proves that individual ions do not exist in spin states of definite permutation symmetry. In view of the exclusion principle the normal vibrational modes must be such that the motions of neighboring ions are highly correlated in contrast to the molecules of solid methane or solid hydrogen.

(b) Second Moments and the $N-H$ Bond Distance

With the assumption that the ions are ordered so that the $N-H$ bonds point in the $(1,1,1)$, $(\bar{1},\bar{1},1)$, $(1,\bar{1},\bar{1})$, and $(\bar{1},1,\bar{1})$ directions, Van Vleck's formula[6] for the second moment becomes

$$\Delta H_2^2 = \frac{3,645}{32,768}\frac{g^2\beta^2}{r^6}\{1-\tfrac{3}{5}(\lambda_1^4+\lambda_2^4+\lambda_3^4)\}(1-\epsilon)$$

$$+\frac{4}{3}\frac{g'^2\beta^2}{r^6}\{1-(\lambda_1^4+\lambda_2^4+\lambda_3^4)\}(1-\epsilon)$$

$$+\frac{g^2\beta^2}{d^6}\{8.7+28.0(\lambda_1^4+\lambda_2^4+\lambda_3^4)\}+0.1 \text{ gauss.}^2 \quad (7)$$

Here r is the $N-H$ bond distance, g' is the nitrogen gyromagnetic ratio, d is the unit cell size, and λ_i is the direction cosine of the external field with respect to the ith cubic axis. The factor $(1-\epsilon)$ takes into account[1] the torsional oscillation of the ammonium ion. The first two terms in Eq. (7) give the intra $-NH_4^+$ interactions. The third term represents the interactions between neighboring NH_4^+ ions; the coefficients were computed[1] assuming $r/d = 1.040/3.820$. The 0.1-gauss^2 term is the broadening from the chlorine and nitrogen nuclei outside a given NH_4^+ ion.

The experimental second moments at low temperature, given in Table I, when substituted in Eq. (7) result in $N-H$ distances of 1.031 ± 0.007 and 1.033 ± 0.004A for the $(1,0,0)$ and $(1,1,0)$ orientations, respectively. These values are in excellent agreement with the neutron diffraction values[5] of 1.03 ± 0.02A. This agreement, as well as the agreement of the values for the two different crystal orientations, confirms the orientation assumed for the NH_4^+ ion in the unit cell.

[13] F. Reif and E. M. Purcell, Phys. Rev. 91, 631 (1953).

5. ABSORPTION IN NH₄Cl ABOVE THE LINE-WIDTH TRANSITION TEMPERATURE

(a) Room Temperature Results

Above $-125°C$ the line width is anisotropic but very slowly varying up to room temperature. The theory given in Sec. 3 is no longer applicable as the measured second moments are consistent with the assumption that the line broadening is due solely to interionic interactions.

Even these interactions are affected by the motion of the ions, and one can try using the dependence to investigate the motion. The second moment in general has the form

$$\Delta H_2^2 = g^2\beta^2d^{-6}\{c_1(\lambda_1^4+\lambda_2^4+\lambda_3^4)-c_2\}+0.1 \text{ gauss}^2, \quad (8)$$

where the second term is an estimate of the contributions of the nitrogen and chlorine nuclei. The angular dependence of this term has been neglected.

Three models were considered. In model a each proton is distributed with equal probability over the four vertices of the tetrahedron; in model b each proton is distributed with equal probability over the four vertices of the tetrahedron as well as over the four vertices of the inverted tetrahedron. In model c each proton is distributed uniformly over the sphere circumscribing the tetrahedron.

Table VIII contains the values of c_1 and c_2 calculated for each model. The observed values at room temperature of c_1 and c_2 were obtained by varying the data, given in Table I for the different crystal orientations, within the limits set by experimental errors so as to obtain a completely consistent set of values of c_1 and c_2.

TABLE VI. Energy levels when external field is along an edge or a C_2 axis.

State in LSIM representation	Energy
$\langle1122\|$	$2g\beta H$
$I = S_{11}\langle1121\|-S_{12}\langle1111\|$	$g\beta H+\frac{1}{4}(A_{12}+A_{34})+h$
$II = S_{12}\langle1121\|+S_{11}\langle1111\|$	$g\beta H+\frac{1}{4}(A_{12}+A_{34})-h$
$\langle1011\|$	$g\beta H-\dfrac{A_{12}}{2}$
$\langle0111\|$	$g\beta H-\dfrac{A_{34}}{2}$
$\langle0000\|$	0
$III = \dfrac{1}{\sqrt{2}}\{\langle1120\|-\langle1100\|\}$	$\dfrac{3}{2\sqrt{2}}(A_{12}+A_{34})$
$II' = \dfrac{1}{\sqrt{2}}\{\langle1120\|+\langle1100\|\}$	$-\dfrac{3}{2\sqrt{2}}(A_{12}+A_{34})$
$\langle0110\|$	A_{34}
$\langle1010\|$	A_{12}
$\langle1110\|$	$-(A_{12}+A_{34})$

If $A_{12}=A_{34}$, $S_{11}^2=1$ If $A_{12}=-2A_{34}$, $S_{11}^2=\dfrac{81}{162+2(82)^{\frac{1}{2}}}$

$S_{12}=0$ $S_{12}^2=1-S_{11}^2$

$h=\frac{1}{4}\{10(A_{12}-A_{34})^2+4A_{12}A_{34}\}^{\frac{1}{2}}$

A comparison of the values in Table VIII makes it clear that the second moment is not very sensitive to the nature of the motion taking place. However, subject to this limitation the room temperature second moments show that not only is the crystal disordered but that the frequency with which an ordered ion becomes a disordered ion (or *vice versa*) is greater than the frequency associated with the line width, which is about 10^5 cps.

(b) Results in the Vicinity of the λ Point

The great changes in the crystal in the vicinity of the λ point are accompanied by almost negligible changes in the absorption. The disordered model b shows a larger line width than the ordered model a because in the disordered crystal the average proton-proton distance is smaller. However, when the crystal becomes disordered, it also expands anomalously[14] and the second moment is sensitive to the size of the crystal through the factor d^6. The two effects almost cancel so that the line width increases only slightly through the phase transition.

However, Eq. (8) can be applied to the observed second moments given in Table I for temperatures just below and above the λ point. With 3.84 and 3.85A assumed for the unit cell sizes,[14] c_1 and c_2 values of 30.5 and 5.3 are found below the phase transition and 32.6 and 5.9 above. The experimental errors are such that these results are not conclusive in themselves, but upon comparison with the theoretical values in Table VIII they provide an interesting confirmation of the order-disorder process.

TABLE VII. Intensities of the lines in the edge or C_2 orientations.

$\Delta E = \pm (E_M - E_{M-1} - g\beta H)$	Relative intensity
$\pm[\frac{1}{4}(A_{12}+A_{34})+h]$	$\frac{1}{4}S_{11}^2$
$\pm[-\frac{1}{4}(A_{12}+A_{21})+h]$	$\frac{1}{4}S_{12}^2$
$\pm\left[\left(\frac{1}{4}-\frac{3\sqrt{2}}{2}\right)(A_{12}+A_{34})+h\right]$	$\frac{3}{16}S_{11}^2$
$\pm\left[\left(\frac{1}{4}+\frac{3\sqrt{2}}{2}\right)(A_{12}+A_{34})+h\right]$	$\frac{3}{16}S_{11}^2$
$\pm\left[\left(\frac{1}{4}+\frac{3\sqrt{2}}{2}\right)(A_{12}+A_{34})-h\right]$	$\frac{3}{16}S_{12}^2$
$\pm\left[\left(\frac{1}{4}-\frac{3\sqrt{2}}{2}\right)(A_{12}+A_{34})-h\right]$	$\frac{3}{16}S_{12}^2$
$\pm[(5/4)(A_{12}+A_{34})+h]$	$\frac{1}{4}S_{12}^2$
$\pm[(5/4)(A_{12}+A_{34})-h]$	$\frac{1}{4}S_{11}^2$
$\pm\frac{3}{2}A_{12}$	$\frac{1}{8}$
$\pm\frac{3}{2}A_{34}$	$\frac{1}{8}$

If $A_{12}=A_{34}=-\frac{1}{2}g^2\beta^2R^{-3}$, $h=\frac{1}{4}g^2\beta^2R^{-3}$ (C_2 orientation)

If $A_{12}=-2A_{34}=g^2\beta^2R^{-3}$, $h=\frac{(82)^{\frac{1}{2}}}{8}g^2\beta^2R^{-3}$ (edge orientation)

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TABLE VIII. The anisotropy of the second moment, described by the parameters in Eq. (8), computed for three structural models and compared with the room temperature measurements.

	c_1	c_2
Model a (ordered)	30.97	4.86
Model b (disordered)	33.08	5.65
Model c (spherical rotation)	34.56	6.14
Experimental values	33.25	5.88

6. THE LINE-WIDTH TRANSITION AND THE MOTIONS OF THE AMMONIUM ION

The observed variation with temperature of the line widths and second moments for the different crystal orientations suggests that the motions of the NH_4^+ ions are essentially isotropic. There is no significant dependence upon crystal orientation of the character of the line-width transition.

The change in line width with temperature was calculated for the (1,0,0) and (1,1,0) crystal orientations using the same procedure, frequency factor (ν_0), and activation energy (E) as for the crystal powder.[1] The line shape factor α was 4.53 for the (1,0,0) and 3.98 for the (1,1,0) orientation. The curves drawn in Fig. 4 give the results of the calculation. The agreement with experiment is reasonably good; certainly there is no significant difference for the two crystal orientations.

The second moments measured along the (1,0,0) and (1,1,0) crystal axes are plotted in Fig. 5 against the temperature. An analysis of these data discloses the general nature of the motions responsible for narrowing the absorption. If we let S_T be the contribution to the second moment at absolute temperature T of the proton-proton interactions on a given NH_4^+, then it is found that S_T/S_0 is independent of crystal orientation, within experimental error. In Fig. 5, the curve drawn through the transition for the (1,0,0) orientation was calculated from the S_T/S_0 values for the (1,1,0) orientation. S_T is given by $(\Delta H_2^2)_T - (\Delta H_2^2)_{233°}$.

The independence of S_T/S_0 upon orientation can be derived by considering the motion of an NH_4^+ ion during the time required for rf absorption. In particular, assume a model in which any given edge of the ammonium ion tetrahedron is at its initial position a fraction $(1-5a)$ of the absorption period and a fraction a at each of the other five possible positions, i.e.,

$$A_{ij}=(1-5a)A_{ij}^0+a\{\textstyle\sum_{k<l}A_{kl}^0-A_{ij}^0\}$$
$$=(1-6a)A_{ij}^0 \quad (9)$$

where A_{ij}, defined as for Eq. (1), is understood to be averaged over the motion of the ion and A_{ij}^0 is the value of A_{ij} when no motion occurs. Also, we have[6]

$$S_T=(9/4)\textstyle\sum_{i<j}A_{ij}^2=(9/4)(1-6a)^2\sum_{i<j}A_{ij}^{0\,2},$$

and

$$S_0=(9/4)\textstyle\sum_{i<j}A_{ij}^{0\,2}.$$

Therefore, we obtain the result, which is independent of

orientation, that

$$S_T/S_0 = (1 - 6a)^2. \qquad (10)$$

An equivalent physical description of this model is the following. A given ion spends a certain fraction of its time in a nonrotating low-energy state. During the remaining time it is randomly excited to states with higher energy in which reorientations occur. These reorientations must produce in the high-energy state a uniform spatial distribution of the ion among the possible orientations in order to give the isotropic result of Eq. (10). The temperature dependence of the second moment arises from the larger fraction of time spent in the high-energy states at higher temperatures.

A crude classical picture is that the ion undergoes a Brownian motion from one equilibrium configuration to all other equilibrium configurations with the same probability. We infer that the state or states in which line narrowing occurs must lie above most of the potential barriers of the system. The same conclusion was reached in the preceding paper[1] by a comparison of the potential barriers deduced from the torsional frequency and from the variation of line width and relaxation time with temperature. Finally we note that the isotropy of S_T/S_0 implies that only one correlation time τ_c is important for this frequency range.

7. ACKNOWLEDGMENT

Electron Spin Resonance in Metals at Low Fields*

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(Received March 25, 1954)

KIP, Kittel, and co-workers have observed electron spin resonance in sodium[1] and in lithium[2] metal at microwave frequencies and at 300 Mc/sec.[3] Measurements on these metals at lower frequencies have been made by Carver, Holcomb, and Slichter.[4] We wish to report the results of some independent observations, at frequencies near 25 Mc/sec, of the absorption line shapes for lithium from 77° to 300°K and for sodium from 77° to 385°K.

The apparatus was identical to that employed for broad nuclear magnetic resonance lines[5] except for two concentric pairs of Helmholtz coils which provided the main magnetic field (0 to 25 gauss) and the field modulation. The system was calibrated by means of the electron spin resonance in α, α-diphenyl β-picryl hydrazyl. The lithium and sodium samples were dispersions prepared by high-speed stirring of the molten metal in mineral oil; particle sizes ranged from 1 to 50μ, averaging 15μ.

The observed derivatives of the absorption lines were recorded automatically as a function of applied magnetic field at a fixed radio-frequency. They are Lorentzian in shape but distorted somewhat on the low-field side. This distortion can be attributed in part to the use of a resonance frequency less than the total half-width of the absorption. Thus, there is still absorption at zero applied field; moreover, absorption occurs from each of the opposing circularly polarized components of the oscillating rf field. Becker and Eisner[6] have reported similar detailed results for the narrower hydrazyl resonance at frequencies less than 3 Mc/sec. Feher and Griswold[3] have pointed out the possible importance of skin effects in distorting the line shape.

In lithium, the resonance at room temperature has a width of 4.4 gauss between the maximum and minimum of the derivative. Widths of 5 gauss have been reported by Feher and Griswold[3] and by Slichter.[4] The Lorentzian line shape suggests that spin-lattice relaxation processes determine the width, which corresponds to a T_1 of 7.5×10^{-9} sec. This relaxation time is shorter by a factor of 10^2 than Overhauser's theoretical prediction.[7] Feher and Griswold[3] have mentioned that the line width increases at lower temperatures; in our sample at 77°K the width was 4.5 gauss, only slightly greater, if at all, than at room temperature.

On the other hand, the width of the resonance in sodium exhibits a pronounced, reasonably linear dependence upon temperature, as shown in Fig. 1. The width decreases from 9.7 gauss at 385°K to 3.6 gauss at 77°K. The slope of 0.018 gauss deg^{-1} gives a width of about 2 gauss when extrapolated to 0°K. The results were independent of the resonance frequency between 20 and 30 Mc/sec. Feher and Griswold[3] reported a width of 10 gauss at room temperature and noted a temperature dependence as well. The different temperature effects for lithium and sodium present an
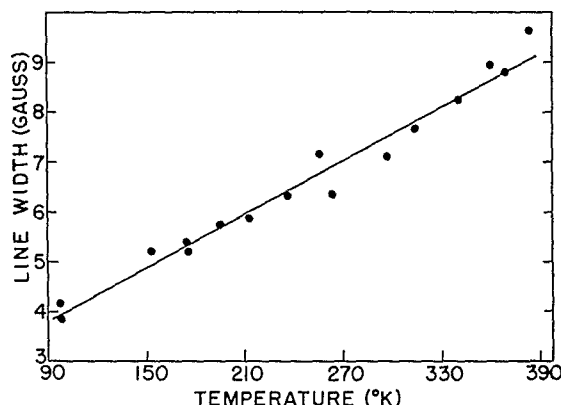

FIG. 1. The temperature dependence of the electron spin resonance absorption in sodium metal dispersed in mineral oil. The line width is defined as the separation between points of maximum slope.

unresolved problem. Overhauser's analysis[7] predicts an increase in T_1 and therefore a decreasing line width with decreasing temperature. The experimental results suggest that T_1 includes a temperature-dependent and a temperature-independent term, the former increasing with nuclear charge. Holcomb and Norberg[8] have found that nuclear relaxation in the metals is sensitive to impurities and imperfections, which could contribute to the electron relaxation.

Electron spin resonance was observed at 77°K in a sample of high-surface sodium prepared by mixing molten sodium with surface-active alumina (Alcoa F-20; 160 meter^2 g^{-1}). The proportions of sodium and alumina were such that if the sodium film was uniform it was 10A thick. The line shape observed is identical with that for the dispersion in mineral oil, confirming that the resonance is from the sodium and not the supporting medium. Unsuccessful attempts were made to detect the electron resonance in K, Rb, Cs, Cu, Be, Mg, Al, Ta, Nb, and V at 30 Mc/sec at room temperature and in K, Rb, Cs, and Mg at 77°K.

* Supported in part by the U. S. Office of Naval Research and by a Grant-in-Aid from E. I. du Pont de Nemours and Company, Inc.
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Proton Magnetic Resonance and Structure of Ammonium Hydroxide*

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(Received July 28, 1954)

IT is conventional to use the formula NH_4OH to represent the molecular state of NH_3 in aqueous solution. This formula is most likely an oversimplification. In fact there is considerable argument against the existence of discrete NH_4OH molecules. Davis[1] has commented on the problem recently, emphasizing the weak noncovalent character of the NH_3-H_2O interaction, and concluding that the system is better described by the equation

$$NH_3+H_2O \rightleftharpoons NH_4^+ + OH^-. \qquad (1)$$
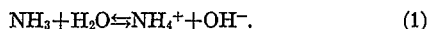
Van Velden and Ketalaar[2] arrived earlier at much the same conclusions.

The experimental evidence is conflicting. Rao[3] found that aqueous ammonia exhibited the same Raman spectrum as liquid NH_3, suggesting no new important molecular species are present in solution. But the infrared spectra of the solid ammonia hydrates show[4] absorption bands found neither in ice nor in solid NH_3. Early thermodynamic arguments[5] were based on the partition of NH_3 between H_2O and immiscible organic liquids and indicated that half or more of the NH_3 remained free in the aqueous solutions. However, Khakham[6] reinvestigated the problem by this method and found only 5 to 10 percent free NH_3.

An independent method is offered by nuclear magnetic resonance. Chemical shifts in the resonance position are a sensitive indication of differences in the electronic environment of nuclei and have proven useful in studying the structure of other solutions.[7] Figure 1 gives the proton resonance position observed[7] in aqueous NH_3 as a function of concentration, at room temperature and a field of 4200 oersteds.
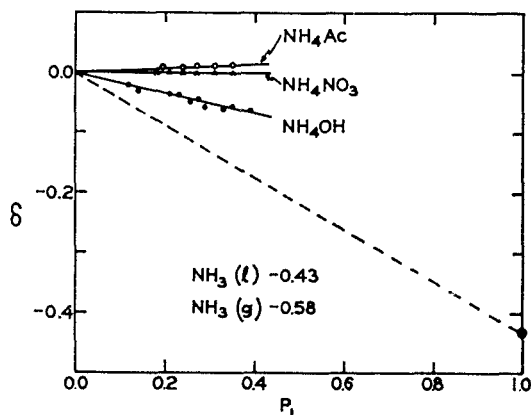

FIG. 1. The position of the proton resonance in aqueous ammonia as it depends on concentration, at room temperature. δ is the shift in resonance position referred to pure H_2O and p_1 is the stoichiometric fraction of protons as NH_3.

The resonance at all concentrations was a single narrow line (<1 millioersted). If discrete molecular species existed with lifetimes longer than about[7] 10^{-3} sec, separate resonance lines would have been found for each species. The conclusion that there is fast proton exchange agrees with the inferences of Eigen[8] and with the unsuccessful attempts[9] to observe directly the exchange rate between D_2O and NH_3.

When chemical exchange produces a single resonance line, its position is a number average of the resonance positions for the nuclei in the absence of that exchange. If Eq. (1) represented the true molecular state of the solutions, the resonance position in the solutions δ_s should be given as[7]

$$\delta_s = p_1\delta_{NH_3} + p_2\delta_{H_2O}, \qquad (2)$$

and defining $\delta_{H_2O} \equiv 0$ as was done experimentally,

$$\delta_s = p_1\delta_{NH_3}. \qquad (3)$$

p_1 is the fraction of the protons in NH_3, and δ_{NH_3} and δ_{H_2O} represent the proton resonance positions of pure NH_3 and H_2O. The small concentrations of NH_4^+ and OH^- are completely negligible in writing Eq. (2).

The observed δ_s values in Fig. 1 are plotted against the stoichiometric p_1. The dotted line represents Eq. (3) using the δ_{NH_3} value from the liquid. The large deviation of this line from the observed data is strong evidence that the structural model of free NH_3 and H_2O is inadequate. Our data show there are significant interactions between NH_3 and H_2O, but the state is a very dynamic one. Eigen[8] has arrived at a similar model from supersonic absorption measurements.

The importance of hydrogen bonding in the solutions is shown by the systematic increase in the δ values of NH_3 (g),[10] NH_3 (l) and the aqueous solutions. However, whether one wishes to describe the state of association as NH_4OH molecules or $NH_3 \cdot H_2O$ complexes seems at this point a matter primarily of personal preference or convention. We are attempting to learn more about the different molecular species actually present, by cooling the solutions to decrease the exchange rate so separate resonance lines can be resolved.

* Supported by the U. S. Office of Naval Research and by a Grant-in-Aid from E. I. duPont de Nemours and Company.
† University of Illinois Post-doctoral Fellow.
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EFFECTS OF RING SIZE ON ELECTRON DISTRIBUTION IN SATURATED HETEROCYCLIC COMPOUNDS[1]

Sir:

Measurements of the basicities of cyclic imines toward trimethylboron,[2] of cyclic ethers toward chloroform and methanol-d,[3,4] and of cyclic sulfides toward boron trifluoride,[5] have shown that the basicity changes with ring size in the order: 4 > 5 > 6 > 3-membered rings. Two differing interpretations of these observations have been suggested.

An interpretation based on steric factors was proposed by Brown and Gerstein[2] to account for the dissociation of the addition compounds of the cyclic imines with trimethylboron. According to this view the observed order of basicity results from a combination of F-strain which is more pronounced for the larger rings, and I-strain which is most important in the 3-membered ring. These strains are considered to be steric interactions which occur because of the association between donor and acceptor molecules.

On the other hand, steric factors alone do not account adequately for the results of the hydrogen bonding studies with cyclic ethers[3,4] nor are they a likely explanation for the interaction of cyclic sulfides with boron trifluoride.[5] It was suggested that the basicity differences were due rather to differences in electron availability caused *inherently* by the different sizes of the rings—that is, the electron distribution is altered by ring size.

Direct physical evidence that the electron distribution does depend significantly on ring size has now been obtained by observing the chemical shifts in the proton magnetic resonance[6] of the cyclic imines, ethers and sulfides. These shifts are a sensitive measure of differences in the electronic environment of nuclei. The δ-values[6] observed for the cyclic compounds are given in Table I, and it is seen that there are relatively large variations with ring size for the hydrogens in both the α and β CH_2 groups.

In each series of cyclic compounds, the δ-values

TABLE I

PROTON MAGNETIC RESONANCE SHIFTS IN SATURATED HETEROCYCLIC COMPOUNDS

Compound	δ-Value[a]	
	α-CH_2	β-CH_2
$(CH_2)_2O$	−0.26	
$(CH_2)_3O$	− .06	−0.25
$(CH_2)_4O$	− .17	− .34
$(CH_2)_5O$	− .16	− .39
$(CH_2)_2S$	− .23	
$(CH_2)_3S$	− .19	− .19
$(CH_2)_4S$	− .29	− .29
$(CH_2)_5S$	− .29	− .34
$(CH_2)_2NH$	− .37	
$(CH_2)_3NH$	− .23	− .16
$(CH_2)_4NH$	− .19	− .30
$(CH_2)_5NH$	− .25	− .36

[a] The assignments of lines to the α- and β-CH_2 groups usually could be made from their relative intensities. There are some uncertainties in values for the cyclic imines because the N–H proton resonance was not always resolved from the CH_2's.

of the 3-membered rings are consistently among the most negative while the α-CH_2's in the 4-membered rings are among the most positive. It has been established[6] that more positive δ-values correspond to lower electron densities about the proton. Also, a low electron density on the CH_2 groups must be compensated for by a high electron density on the hetero atom. So we conclude that the hetero atom has a low electron density in the 3-membered ring and high in the 4, which agrees with the observed order of basicity.

It is also noteworthy that the changes in electron distribution with ring size appear to be more systematic at the β-CH_2 group than at the α. As the ring size increases, the δ-value for the β-CH_2 group approaches monotonically the value −0.39 observed in cyclohexane.[6]

Further study of variations in electron distribution with ring size is planned with these and other systems. More detailed data and interpretations will be presented.

(1) This work was supported by the Office of Naval Research and by a Grant-in-Aid from E. I. du Pont de Nemours and Company.

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